GEOCHEMICAL INTERPRETATION OF

OCCURRENCE OF NITRATE IN

GROUNDWATER

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by

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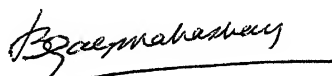
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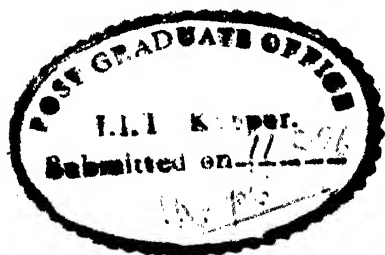
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Abstract

This thesis summarizes geochemical interpretation of a CGWB data base on the occurrence of high (> 45 mg/L) levels of nitrate in ground water within the alluvial plain of Uttar Pradesh. Standard statistical techniques like determination of correlation coefficient and factor analysis did not reveal any strong association of nitrate with other dissolved constituents. For example, the correlation cofficients had low positive values in the decreasing order :

$$SO_4(0.524) > Mg(0.522) > Na(0.447) > HCO_3(0.341) \cdots$$

$$\cdots > SiO_2(0.308) > Ca(0.297) > Cl(0.281) > K(0.243)$$

Only F^- had a low negative value (-0.161) which can be explained by its inverse relationship with Ca^{2+} controlled by dissolution of Ca-F minerals like fluorite or apatite. It also appears that nitrate derived from anthropogenic sources like fertilizer application and domestic sewage occurs in association with costituents like Na, Mg, Cl, SO_4, HCO_3 derived from alkali soils of that area.

Once nitrate enters into ground water, it undergoes denitrification at two ranges of vertical depth. In the vadose zone, biological reduction of nitrate is favoured by abundance of soil organic matter. Upto a depth to water table of around 10 m, NO_3 concentration rises sharply with depth due to lack of denitrification with decreasing organic matter content. This trend matches with that observed in the shallow dug-wells within Deccan Trap Hydrologic Province of Maharashtra.

When the depth to water is around 25 m, a reverse trend of lower nitrate at greater depth is observed which can be explained by non-microbial (mineralogical) denitrification by oxidizable Fe-minerals in the aquifer like garnet, hornblende and pyrite. The

redox relationship among disolved nitrogen species has been depicted by P_{O_2}-pH and Eh-pH diagrams.

Spot checks in the IITK area showed that the maximum NO_3^- value of 36.6 mg/L occurred in a shallow dug-well within a village while deeper tube-wells had relatively lower values. This pattern of migration of nitrate ion through soil zone is in contrast with phosphate fixation by soil clays. Controlled laboratory experiments confirmed that lateritic soil, which is efficient in PO_4^{3-} uptake, fails to adsorb NO_3^- under similar conditions although it is also an anion. This difference in behaviour can be explained by the molecular structure of PO_4^{3-} and NO_3^- ions.

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Chapter 1

Introduction and Objective

The study of nitrate in natural waters has now become an inter-disciplinary investigation. As Gayle et al.(1989) have pointed out, this constituent of surface and subsurface water has drawn the attention of agronomists, soil scientists, limnologists,hydrologists and microbiologists. Based on their findings on denitrification in natural systems, environmental scientists and engineers have developed various methods for removal of undesirable levels of nitrate from water.

A change in agricultural practice in many countries has led to an increasing use of nitrogenous fertilizers on land. A good part of the nitrogen applied ends up as nitrate in river and groundwater. Once this nitrate enters drinking water supplies, it can cause serious health hazards, mainly infantile methaemoglobinaemia (blue baby disease) and stomach cancer. High nitrate is also harmful in some industrial processes such as cement and concrete making(Das et al.,1981).

Nitrate is a prime nutrient and rising concentrations might be expected to increase eutrophication of waters. Croll and Hayes (1988), while studying the nitrate pollution of waters in the U.K., found that eutrophication due to nitrates was not evident in most inland waters as phosphorus is usually the limiting nutrient. However, nitrate-induced

eutrophication was observed in coastal waters.

1.1 Acceptable levels in water

The maximum acceptable levels of nitrate in water are mainly determined by a need to prevent physiological damage. A level of less than 50 mg/L nitrate (11.3 mg/L $NO_3^- - N$) [1] was recommended by W.H.O.(1970) and was adopted as the maximum admissible concentration of nitrates in drinking waters by the I.C.M.R. and the EEC. W.H.O.(1984) guidelines set the acceptable limit at 45 mg/L nitrate (10 mg/L $NO_3 - N$),the lowest level at which methaemoglobinaemia had been observed.

1.2 Nitrogen Cycle

As seen from Figure 1.1, nitrogen occurs in natural waters in -3 to +5 oxidation states. NH_4^+, NO_2^- and NO_3^- are the most important among them and NO_3^- is the most stable, being the end product of the oxidation of nitrogenous compounds in water.

The following explanation of the nitrogen cycle was given by Sawyer and Mc-Carty(1967). Plants and certain bacteria can take up nitrogen in the form of nitrates or ammonia and convert it into proteins in the presence of sunlight, whereas animals depend upon plants or other animals that feed upon plants for their protein requirement.

Urine and nitrogenous fertilizers contain nitrogen principally as urea, which is hydrolyzed rapidly by the enzyme urease to ammonium carbonate.

$$(NH_2)_2CO + 2H_2O \xrightarrow{\ urease\ } (NH_4)_2CO_3 \tag{1.1}$$

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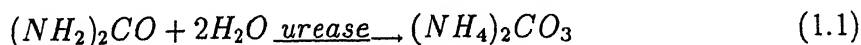
[1] 50 mg/L $NO_3 = 50 \times \frac{atomic\,wt.\,of\,N}{Molecular\,wt.\,of\,NO_3^-}$ mg/L $NO_3 - N = 50 \times \frac{14}{62} = 11.3$ mg/L $NO_3 - N$
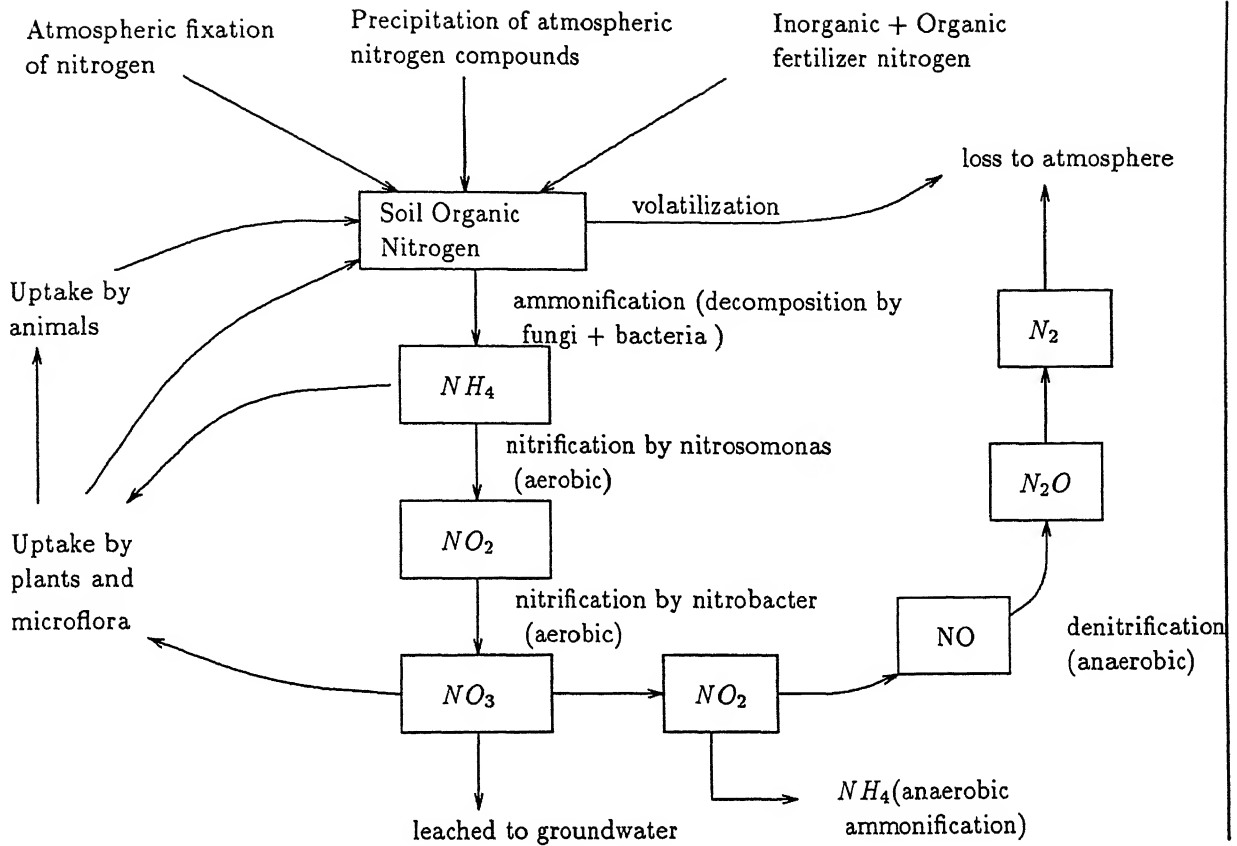
Figure 1.1: Nitrogen Cycle

Faecal protein matter and protein from decomposed plants and animals are converted to ammonia by the action of saprophytic bacteria under either aerobic or anaerobic conditions.

$$Protein(organicN) \xrightarrow{saprophytes} NH_3 \qquad (1.2)$$
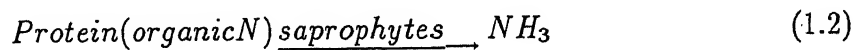
The ammonia released by bacterial action on urea and proteins may be used by plants directly to produce plant protein. The excess NH_3 is oxidized by autotrophic nitrifying bacteria.

$$2NH_3 + 3O_2 \xrightarrow{nitrosomonas} 2NO_2^- + 2H^+ + 2H_2O \qquad (1.3)$$

$$2NO_2^- + O_2 \underline{\textit{nitrobacter}} \longrightarrow 2NO_3^- \qquad (1.4)$$
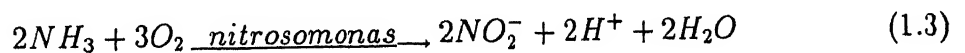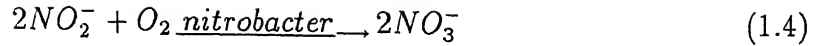
The nitrates formed are taken up by plants and the excess nitrates are carried down to the water table by percolating water, frequently resulting in high nitrate concentrations of groundwater.

Under anaerobic conditions, denitrifying bacteria oxidize organic matter for energy while reducing nitrates and nitrites to nitrogen gas.

$$4NO_3^- + 5CH_2O \underline{\textit{denitrifiers}} \longrightarrow 2N_{2(g)} + 5HCO_3^- \qquad (1.5)$$
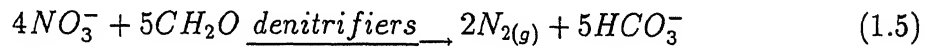
The nitrogen gas produced escapes to the atmosphere.

1.3 Importance of Aquifer Properties

Nitrate is easily leached down to the water table with infiltrating water. The nitrate concentration of groundwater depends on a number of aquifer properties such as:

- Mineralogy of the aquifer(presence of ferrous iron, pyrites, etc.),

- presence of organic carbon in the aquifer and in the unsaturated zone above the water table,

- the presence of dissolved oxygen.

The depth of water table was shown to affect the concentration of nitrate in groundwater since denitrification is inactive at greater depths in the absence of organic carbon in the Deccan Trap Hydrologic Province (Pawar and Shaikh, 1995). Mixing of groundwaters of different origins may also cause attenuation of nitrate levels in groundwater

samples, as shown by Howard (1985).Nitrate pollution of groundwater may be thus controlled naturally where the aquifer conditions favour denitrification or the inorganic reduction of nitrate to nitrogen gas. The falling levels of nitrates with increasing depth to water table in some areas may be explained by the presence of a *redoxcline*, below which anaerobic conditions favour nitrate reduction.

1.4   Objective

Based on the status of geochemical data on the occurrence of nitrate in groundwater as summarised above, the present work was carried out with the following objectives.

1. To select a water quality data base containing information on high nitrate groundwater in the alluvial plains of U.P.

2. To interpret the data in terms of standard statistical parameters like correlation coefficient,factor loading, etc. and thereby decipher possible relationships between nitrate and other dissolved ions.

3. To evaluate the control of redox reactions in the aquifer with the help of Eh-pH diagram, nitrate-depth relations and samples collected from local open wells and tube wells.

4. To compare the data from alluvial aquifers with those reported from hard-rock terrains e.g. Deccan Basalt of Maharashtra.

5. To verify the reported lack of adsorption of NO_3^- ion in soils by controlled laboratory experiments and to compare and contrast these results with earlier work on phosphate adsorption.

Chapter 2

Literature Review

2.1 Source of Nitrate in Groundwater

The main source of nitrate in groundwater seems to be the use of nitrogenous fertilizers for intensive cultivation. High nitrate values in groundwater at several locations in Uttar Pradesh were attributed to faulty soil, water, and fertilizer management practices (Adarsh Kumar,1983).Pawar and Shaikh(1995) found high values of nitrate (upto 64 ppm) in basaltic aquifers of the Deccan Traps. These high values coincide with irrigated sugarcane fields and indicate fertilizers as the main source of nitrate pollution. Nightingale (1970) had concluded that water from agricultural zone shows a greater increase in nitrate concentrations than that from urban zone.

Urbanization involves the disposal of sewage wastewater, which on percolating through soil ultimately reaches the water table. Human and animal wastes contain organic nitrogen, which on oxidation is converted to nitrate and is easily leached down to the water table (Hamill and Bell, 1986).Upto 90 percent of the original content of nitrogen in secondary effluent of wastewater may be removed by filtering through soil. The nitrogen not removed from water will eventually reach the water table as either NO_3^- or NH_4^+, depending upon the amount of oxygen available (Lance, 1972). Onsite

sewage disposal systems cause an increase in the concentration of nitrate-nitrogen in the recharge water. The nitrate impacts on groundwater can be predicted by mass-balance, considering input from wastewater and recharge of rainfall (and snowmelt) over a defined geographic area and losses due to denitrification in soil column and the aquifer. The acceptable development densities or the carrying capacity of land for land-use planning can be calculated from the nitrate impact (Hantzsche and Finnemore, 1992).

Thus, anthropogenic sources may be another important cause of nitrate pollution. A few other sources of nitrate in water may be:

- Atmosphere : Atmospheric nitrogen is oxidized to N_2O_3 during lightening discharges in storms. N_2O_3 reacts with water to form HNO_3, which is carried to the earth by rainwater (Sawyer and McCarty, 1967). Certain leguminous plants fix atmospheric nitrogen in soil at their root zones forming a potential source of nitrate pollution.

- Buried Organic Nitrogen : The remains of plants and animals buried and trapped under soil layers may also be regarded as potential nitrate pollutants for groundwater (Das et al., 1981). Natural soil nitrate, generated by the oxidation of organic nitrogen in the root zone of grasslands and leached down by infiltrating water, has accumulated in the soil profile of Runnels County, Texas and is the main cause of nitrate pollution in that region (Kreitler and Jones, 1975).

- Geologic Sources : Some constituents of the geologic environment may also contribute to the nitrate in groundwater, but the nitrate concentrations obtained from parent rock of aquifers is too low to cause severe contamination (Henderson, 1982). However, nitrates derived by the oxidation of ammonium present within the weathered glacial tills of Southern Alberta, Canada greatly increased

the nitrate concentration of well-waters in a few enclaves. These ammonium-rich enclaves were originally formed when ammonium replaced the exchangeable potassium in clay minerals (Hendry et al., 1983). Alkali soils (e.g. reh) may be associated with nitrates, which can redissolve during the rainy season and seep down to the water table. (Krishnan, 1960).

2.2 Identification of Source of Nitrate Pollution

Natural variations of N-isotopes can be used to identify the source of nitrate in groundwater. Unique isotopic ranges for nitrate from different environments were delineated and were compared to the nitrogen isotope ratios of groundwater nitrate to determine the predominant source(Kreitler and Jones, 1975; Gormly and Spalding, 1979; Hendry et al., 1983). The stable isotopes of nitrogen are ^{14}N and ^{15}N. 99.632 $\pm$ 0.002 percent of nitrogen in the atmosphere is ^{14}N (Kreitler and Jones, 1975). In other nitrogenous compounds, these percentages vary slightly because of isotopic fractionation. The variations of mass are measured on a gas-source mass-spectrometer in which the sample is compared to atmospheric nitrogen standard. The ratio of sample to standard is expressed in the accepted isotopic terminology as :

$$\delta^{15}N(permil) = \frac{\left(\frac{^{15}N}{^{14}N}\right)_{sample} - \left(\frac{^{15}N}{^{14}N}\right)_{standard}}{\left(\frac{^{15}N}{^{14}N}\right)_{standard}} \times 1000 \qquad (2.1)$$

A similarity between the pattern of chloride and nitrate concentrations was observed in groundwater samples from the Deccan Trap region (Pawar and Shaikh, 1995). High nitrate with high Cl indicated a common fertilizer source, on the other hand high Cl with low NO_3^- indicated non-fertilizer (domestic sewage) source. Das et al.,(1981) prepared an index of the extent of groundwater pollution in parts of M.P. and U.P.

using NO_3^- concentration and K/Na mole ratios. The results revealed that most of the shallow dug-wells which were grossly polluted had high values of NO_3^- and K/Na mole ratios.

2.3 Health Hazards from Nitrate in Water

Das et al., (1981) mention that Comley was the first to recognize in 1945 that water containing high nitrate is toxic in effect for human consumption and is not suitable for drinking, particularly by infants upto the age of six months. Water containing high nitrate affected young bottle-fed babies by causing infantile methaemoglobinaemia, a disease commonly known as 'blue-baby disease' or 'water-well cyanosis', which causes blue colouration of the skin. This may sometimes prove fatal. Nitrate is reduced to nitrite in the stomach and is then absorbed into the blood stream, causing reduction of haemoglobin present in blood to methaemoglobin. This compound deprives the body tissues of oxygen and results in suffocation. Nitrate is more likely to be bacterially reduced to nitrite in the digestive tract of infants since the gastric juice of unweaned infants is less acidic (approaching neutrality) than that of adults (Adarsh Kumar, 1983). Nitrites on combination with amines form nitrosamines, which may cause gastric cancer in humans (Cotton and Wilkinson, 1982). Nitrosamines may also cause mutations and congenital malformations in humans (Starr and Gillham, 1993). Recent literature , however, indicates that there is a controversy as to whether or not high nitrate concentrations in drinking water cause infantile methaemoglobinaemia and gastric cancer (Hiscock et al., 1991). Conflicting conclusions of epidemiological techniques show that nitrate may not be the only cause of these diseases.

2.4   Denitrification in soil and aquifer

Soils contain an abundance of denitrifying bacteria that can use nitrate in the absence of oxygen to convert organic carbon into energy. For bacterial reduction of nitrate, the water must contain an energy source which can be oxidized under anaerobic conditions. Denitrification is defined as the dissimilatory reduction by essentially anaerobic bacteria, of one or both of the ionic nitrogen oxides (NO_3^- and NO_2^-) to the gaseous oxides (NO and N_2O) which may themselves be further reduced to dinitrogen (N_2). Denitrification is catalyzed by either heterotrophic or autotrophic bacteria that derive their energy requirement by the oxidation of organic and inorganic material, respectively. Examples of heterotrophic denitrification are :(Gayle et al.,1989)

$$5CH_2O\,(carbohydrate) + 4NO_3^- + 4H^+ \;=\; 2N_2\uparrow +5CO_2\uparrow +7H_2O$$

$$5CH_3OH\,(methanol) + 6NO_3^- + 6H^+ \;=\; 3N_2\uparrow +5CO_2\uparrow +13H_2O$$

$$5C_2H_5OH\,(ethanol) + 12NO_3^- + 12H^+ \;=\; 4N_2\uparrow +10CO_2\uparrow +21H_2O$$

$$5CH_3COOH\,(acetic\,acid) + 8NO_3^- + 8H^+ \;=\; 4N_2\uparrow +10CO_2\uparrow +14H_2O$$
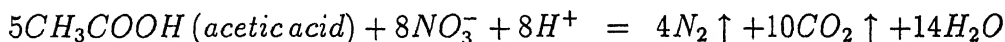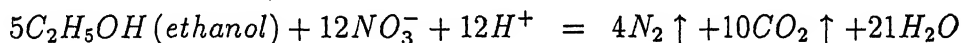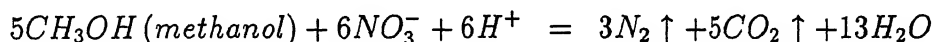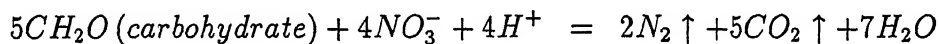
Gaseous organic substrates such as methane and carbon monoxide can also be used as substrates for denitrification.

Autotrophic denitrificaton is a process in which hydrogen or reduced sulphur compounds are used as energy sources instead of organic carbon :

$$Hydrogen:\; 2NO_3^- + 5H_2 + 2H^+ \;=\; N_2\uparrow +6H_2O$$

$$Thiosulphate:\; 5S_2O_3^{2-} + 8NO_3^- + H_2O \;=\; 4N_2\uparrow +10SO_4^{2-} + 2H^+$$

$$Sulphide:\; 5S^{2-} + 8NO_3^- + 8H^+ \;=\; 5SO_4^- + 4N_2\uparrow +4H_2O$$
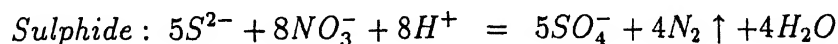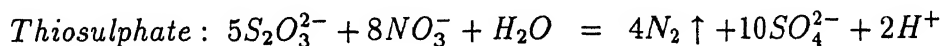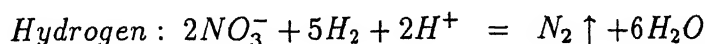
Nitrate concentrations in shallow groundwater of a limestone aquifer were observed to decline with a corresponding decline in dissolved oxygen concentration and an increase in the bicarbonate concentration (Trudell et al.,1986).

$$4NO_3^- + 5CH_2O = 2N_2 + 2H_2O + 5HCO_3^- + H^+$$

$$5CaCO_3 + 5H^+ = 5Ca^{2+} + 5HCO_3^-$$

$$\overline{4NO_3^- + 5CH_2O + 5CaCO_3 + 4H^+ = 2N_2 + 10HCO_3^- + 5Ca^{2+} + 2H_2O}$$
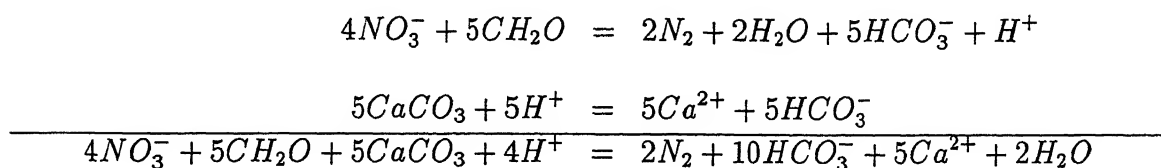
The calcium carbonate was derived from the calcareous soils of the region studied. Through the leaching of ammonium nitrate under field conditons, nitrification and nitrate reduction were shown to be simultaneously occurring in the sandy soil of Bhubaneshwar (Mishra and Misra, 1991). Significant capacity for insitu nitrate reduction in the Lincolnshire limestone aquifer of U.K. was found due to the presence of pyrite and ferrous minerals in the aquifer (Edmunds and Walton, 1983). In deeper aquifer systems, input of organic carbon from the soil reservoir is unimportant and so the likely source of degradable organic carbon is the geologic material comprising the aquifer matrix (Bradley et al.,1992). Riparian forests dominated by wetlands are known to attenuate the nitrate levels of groundwater to a great extent. A greater proportion of groundwater borne NO_3^- in these forests moves within the biologically active zone of the soil and is susceptible to uptake by plants and microbes (Nelson et al.,1995). The spatial and temporal variation in groundwater nitrate removal proved that riparian zones dominated by well drained soils may be less effective than those dominated by poorly drained soils and that microbial processes such as immobilization and denitrification were responsible for much of the observed groundwater NO_3^- removal rather than plant uptake.

2.5   Factors affecting Denitrification

Oxygen, which competes with nitrate as an electron acceptor, is an important inhibitor of denitrification. The gradual depletion of oxygen or the provision of microaerophilic (semi-anaerobic) conditions appears to favour denitrification. This explains the simultaneous occurrence of nitrification and denitrification in the unsaturated zone of soil (Mishra and Misra, 1991). Trudell et al.,(1986) provide evidence of denitrification in a shallow unconfined aquifer in Ontario, Canada. The aquifer, lying within an organic rich wetland environment, consists of fine brown and grey sands with a water table at 1.0 m depth. Tracer experiments with nitrate and bromide showed that nitrate concentration declined at a greater rate than could be explained by simple dilution in a zone between 1.5 and 2 m depth. An assay of soil samples indicated populations of both, autotrophic and heterotrophic denitrifiers present below the water table, maintaining a denitrification rate of between 0.2 and 3.1 mg N/L/d. A striking similarity was observed in the nitrate and dissolved oxygen concentration profiles. The loss of nitrate was preceded by a decline in DO concentration to less than 0.1 mg/L. The measured available DOC is in the range 1.0-3.0 mg/L, except for one sample at a depth of 2.1 m, which recorded 12.4 mg/L. The carbon source is estimated to be soil organic carbon, which, in this reducing environment, at 0.08-0.16% by weight is adequate to denitrify large amounts of nitrate. Experimental evidence demonstrates that nitrate reduction is not observed at an oxygen concentration above 0.2 mg/L (Hiscock et al.,1991).

The availibility of organic C is essential for heterotrophic denitrification. A C:N ratio of 1 is required for 80-90 % denitrification (Hiscock et al.,1991). The dissolved organic carbon (DOC) of groundwater comes from either surface organic matter or originates in the action of bacteria on kerogen, the fossilized organic matter present in

geologic material. In groundwater, the concentration of organic carbon is limited by oxidation of the organic matter to carbon dioxide before reaching the water table, and the general lack of soluble organic carbon contained in aquifer solids. Values of DOC measured for a shallow sand and gravel aquifer suggested a potential for denitrification of only upto 3 mg N/L (Hiscock et al.,1991). Bradley et al.,(1992) attributed the highly significant relation between potential denitrification and sediment total organic content and the enhanced activity of sediments ammended with glucose to the carbon limitation of denitrification rates in an anaerobic groundwater system. It was hypothesized, therefore, that similar processes may limit denitrification in groundwater systems and that these limitations may contribute to the NO_3^- accumulation in anaerobic aquifers. Starr and Gillham (1993) investigated the importance of organic carbon in controlling the occurrence of denitrification in two shallow sandy aquifers in Southern Ontario, Canada and found that denitrification occurred in the aquifer with a very shallow water table, but did not occur in the aquifer with a deeper water table because there was insufficient labile organic carbon present. The denitrification rate was measured using the acetylene block technique. Acetylene inhibits the transformation of nitrous oxide to nitrogen, hence N_2O formation in the presence of acetylene can be used to measure denitrification rates. The concentration of nitrate was observed to increase with depth to water table in the Deccan Trap basaltic aquifers (Pawar and Shaikh, 1995). This was explained by the inactivity of the denitrification process at greater depths in the absence of organic carbon.

Denitrification is positively related to pH with an optimum in the range 7.0-8.0 (Hiscock et al.,1991). Denitrification proceeds slowly below pH 5.5 and below 10^0 C temperature (Lance, 1972). At low temperature, denitrification decreases markedly but is measurable between 0 and 5^0 C. A synergistic effect of temperature and oxygen

upon denitrification can be noted : at a high temperature, oxygen solubility is less, thus increasing the biological rate process, and vice versa. Generally, a doubling of denitrification rate is possible with every 10^0 C increase in temperature (Hiscock et al.,1991).

Several workers have observed a decline in the groundwater redox potential from a highly oxidized state in upland recharge areas to a reduced state after migration to lowland discharge areas under confined flow conditions. The change in redox potential is often accompanied by a sequential reduction in dissolved groundwater species, beginning with oxygen and nitrate, and is often sited as evidence for denitrification. Howard (1985) argues that such evidence should not be taken in isolation as proof of denitrification since other factors, including the spatial and temporal variability of the sources of nitrate and the frequent mixing of groundwaters of different origins, must be considered.

Significant capacity for in situ nitrate reduction in the Lincolnshire limestone aquifer of U.K. was found due to the presence of pyrite and ferrous minerals in the aquifer (Edmunds and Walton, 1983). A redox boundary was found to exist and the complete reduction of oxygen below the boundary suggested a link with the reducing lithology of the aquifer. Resampling of the aquifer after a period of 10 years showed that the redox boundary has become less distinct, representing the presence of small concentrations of nitrate in the absence of oxygen.

Nitrate reduction in deep soil profiles was shown to occur by the chemical oxidation of ferrous iron and reduced sulphur compounds in the aquifer material under anaerobic conditions in the absence of biological denitrifiers (Pedersen et al.,1991). A new term called the TRC (Total Reduction Capacity) of the aquifer was coined. It quantified the total amount of reduced compounds present in the aquifer (ferrous iron, reduced

sulphur compounds,solid organic carbon). The reduction of nitrates by ferrous iron and by sulphide can be represented by :

$$5Fe^{2+} + NO_3^- + 12H_2O = 5Fe(OH)_3 + \frac{1}{2}N_2 \uparrow + 9H^+$$

$$\frac{5}{14}FeS_2 + NO_3^- + \frac{2}{7}H^+ = \frac{5}{7}SO_4^{2-} + \frac{5}{14}Fe^{2+} + \frac{1}{2}N_2 \uparrow + \frac{1}{7}H_2O$$
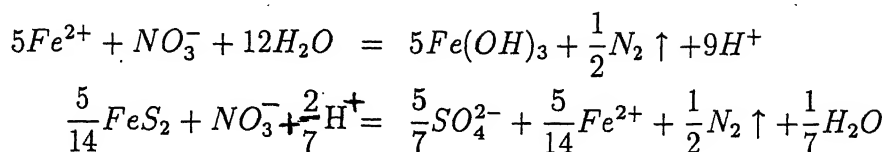
2.6 Artificial removal of nitrate

The methods available for artificial removal of nitrate from water are:

- Artificial Denitrification : Biological denitrification is artificially stimulated by supplying the essential nutrients for biosynthesis in either above ground reactor units or in situ (inside the aquifer). In a third approach denitrification is performed in an above ground reactor and the denitrified water is recirculated underground for filtration and re-aeration. (Hiscock et al.,1991).

- Ion-exchange method : Nitrate is removed from water by treatment with nitrate-selective resins such as IRA 410, Duolite HP555 and Amberlite IRA 996 (Croll and Hayes, 1988; van der Hoek, 1988).

Table 2.1 compares the advantages and disadvantages of both, biological nitrate removal and ion-exchange treatment method.

A further advancement was made by van der Hoek et al.(1988) by combining nitrate removal by ion-exchange and regeneration of the resin with biological denitrification.Murphy (1991) described a chemical process in which Al powder reduces nitrate to ammonia, nitrogen and nitrite. He claimed that with suitable control of pH and dissolved Al, the process is potentially useful. Fritsche (1993) examined several Bi

Characteristic	Ion-exchange treatment	Biological denitrification
Raw water composition	High Cl and sulphate concentrations undesirable Suspended solids not a problem with groundwater.	Little effect Temperature not a problem with groundwater.
Start-up	Immediate	Slow, upto 1 month
Plant complexity	Fixed resin bed process simple and readily amenable to automation, continuous loop process more complex.	Mechanically more complex and more difficult to automate
Process control	Monitoring of nitrate	Monitoring of carbon source, nitrate and nitrite.
Treated water quality	Increased Cl concentration can cause corrosion problems in distribution. Ionic quality variable from fixed-bed process, more constant from continuous-loop process.	Low DO and increased suspended solids. Residual nitrite and carbon source in denitrified water possible.
Further treatment	pH correction may be required.	Reaeration and filtration to remove biomass carry-over.
Waste disposal	Large volumes of spent regenerant and rinse water high in Cl, nitrate and sulphate.	Nitrate transformed into N_2 gas, small volume of biomass sludge.

Table 2.1: Comparison of above-ground denitrification and ion-exchange method (Hiscock et al.,1991)

compounds to remove NO_3^- and other anions from water. He concluded that yellow bismuth hydroxide prepared by the addition of $NaOH$ to Bi_2O_3 dissolved in HCl is suitable for removal of nitrate. The mechanism is ion-exchange with OH^- as counter-ion.

Chapter 3

Materials and Methods

3.1 Statistical Evaluation of Data

Statistical associations among dissolved constituents were investigated using correlation analysis and factor analysis. Correlation coefficients are calculated for all possible pairs of variables. In R-mode factor analysis, a set of few factors is found, that may explain the variance of a large number of analytical data. The factors group together correlated variables, and if they are interpretable, it means that they can be associated directly or indirectly with some specific source or process (Drever, 1988). The R-mode factor analysis program expresses the variables in terms of k factors, the number k being normally much smaller than the number of variables. The factor loadings obtained are a measure of the extent to which each factor is associated with a particular variable. Loadings may have numerical values between +1 and -1. If two loadings on the same factor have the same sign, the variables are positively correlated. The measure of how well the variance of a particular variable is described by a particular set of factors is called the communality. It is usually possible to relate factors that explain a large percentage of the variance to specific sources or processes; factors that explain only a small percentage of the variance commonly have no obvious relationship to identifiable

sources. The FACTOR procedure of the SPSS-X software was used for correlation and factor analysis.

3.2 Adsorption Experiment

The main components of the experiment were natural laterite soil and standard nitrate solutions. Details about these are given below :

3.2.1 Laterite soil

The laterite soil was taken from the collection from Kirkos (1986). The soil had developed over charnockite and biotite gneiss bed rock. Its X-ray pattern showed peaks of kaolinite, gibbsite, goethite and quartz. The red colour was due to iron-oxide or hydroxide. However, as only one X-ray peak of goethite was seen, it was concluded that most of the iron occurred as X-ray amorphous forms (limonite). Other properties of the soil determined by Kirkos (1986) are given below :

Depth from surface level	1.9m
Clay fraction	13.7%
Organic matter content	7.5%
.Soil pH	7.3
CEC	9.6me/100g

3.2.2 Apparatus used

The following apparatus was used to carry out the experiment:

1. Systronics type 335 digital pH meter (Systronics, Naroda, India).

2. Perkin Elmer Lambda-2 UV-vis spectrophotometer (Perkin Elmer, USA).

3. K-12 (Super) Analytical Single Pan Balance (K.Roy and Co., Varanasi,India).

4. Hot air oven (Adair Dutt and Co., Calcutta, India).

5. Type 2LH Magnetic Stirrer (Remi Corporation, India).

6. Debyeflex 2002 (Automatic Powder X-ray diffractometer, (Seifert and Co., USA).

7. Standard laboratory glassware and apparatus.

3.2.3 Nitrate Standards

A nitrate stock solution of 100 ppm was prepared by dissolving 0.18 g of oven-dried KNO_3 in 250 ml distilled water. It was preserved with 0.5 ml chloroform. 10 ppm and 20 ppm solutions and the standard solutions were prepared by appropriate dilution of this stock solution.

3.2.4 Nitrate Analysis

Nitrate in solution was determined by the UV-spectrophotometric Screening method (Standard Methods, 1989). Measurement of UV absorption at 220 nm enables rapid determination of nitrate. The nitrate calibration curve follows Beer's law upto 11 mg/L. A linear relationship was obtained between absorbance and concentration of nitrate in solution by using standard solutions of 2.00, 4.00, 6.00 and 8.00 mg/L. Samples and standards were acidified by 1 N HCl (1 mL HCl added to 50 mL solution) to prevent interference from hydroxide or carbonate concentrations upto 1000 mg $CaCO_3$/L. A typical calibration curve is shown in figure 3.1. Reagent blanks were run and samples were diluted when

required. The absorption value of blank was subtracted from the standard values for calibration.
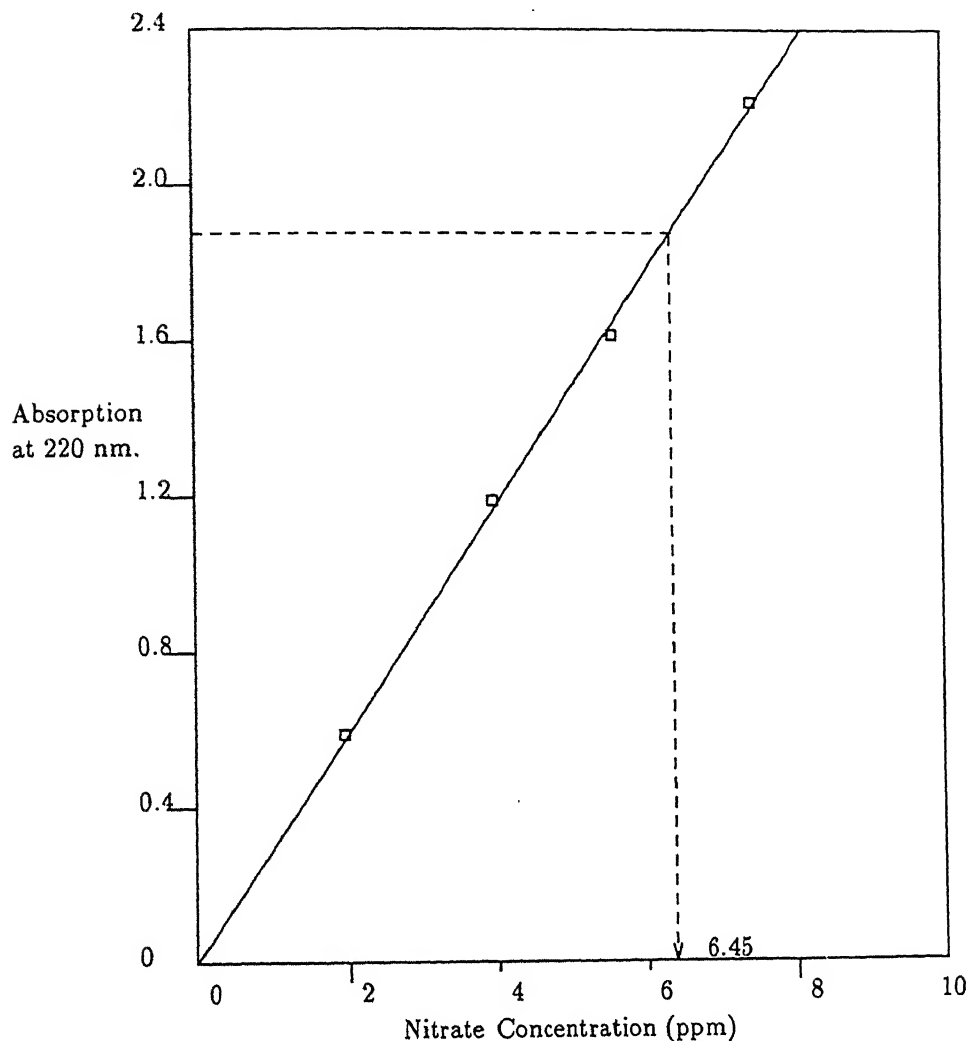
Figure 3.1: A Typical Calibrtion Curve for Nitrate Analysis

3.2.5 Experimental procedure

The soil samples were sieved in the size range -200, +230 ASTM sieves (0.063 to 0.075mm).Weighed amounts of soil were stirred into nitrate solutions of pre-determined concentrations so as to give 1% or 2% suspension and the initial pH was measured. After an equilibrium time of 24 to 76 hours, the suspension was

filtered through Whatman 42 filter paper. Final pH and nitrate were determined in the clear filtrate. Nitrate adsorption was calculated by the difference between initial and final concentration.

3.3   Collection of ground water samples

The samples from dug-wells and tube-wells were collected in clean polyethylene bottles. The tube-well samples were collected after pumping for approximately five minutes. The samples were then brought to the laboratory for measurement of pH and nitrate analysis. The samples were analyzed for nitrate using the UV-spectrophotometric screening method (Standard Methods, 1989).

Chapter 4

Results and Discussion

4.1   Data Base on Groundwater in U.P.

Central Ground Water Board (CGWB) has established a network of hydrograph stations covering the entire state of U.P. Hydrogeological and water quality data from these stations have been compiled into a report titled "Hydrogeological and Hydrochemical Characteristics of Permanent Hydrograph Stations in U.P."(CGWB, 1984). This report contains several sections on chemical analysis of groundwater along with associated data on the geometry of the water table. It has been observed that the nitrate value in most parts of the state is within the W.H.O. limit of 45 mg/L. However, values higher than this limit have also been recorded from several districts. As the main objective of this work is to interpret the factors controlling the occurrence of nitrate in groundwater, these high nitrate values have been reproduced in Table 4.1. It was noted that these samples were collected in the month of April 1982. Annexure II of the same report contains information on the depth to water table during different seasons. In order to be consistent with the chemical analysis data, the depths to water table

in April, 1982 (or June, 1982 where April data were not available) were extracted from this annexure and have been incorporated in table 4.1

The same report also contains detailed information on the location of each well and mentions that all the wells are dug-wells in alluvium. The water quality maps accompanying the report display distribution of residual alkalinity, EC, chloride and fluoride. Therefore, the present information on the distribution of nitrate will be a useful addition.

4.2 Relationship between nitrate and other dissolved constituents

As mentioned in chapter three, the SPSS-X software was used for correlation and for factor analysis. The correlation matrix obtained is given in table 4.2. Except for fluoride, all the other constituents were found to be positively correlated with nitrate. These are arranged in the decreasing order of correlation as :

$$SO_4(0.524) > Mg(0.522) > Na(0.447) > HCO_3(0.341) \cdots$$

$$\cdots > SiO_2(0.307) > Ca(0.297) > Cl(0.281) > K(0.243)$$

Similar low positive correlations between NO_3 and K, Na, SO_4 and Cl was found by Das et al.,(1981) in shallow groundwater within the upper catchment of Betwa river in M.P.-U.P. They explained the lack of correlation between NO_3 and K by the meagre use of K-fertilizers, which may also be true in the present alluvial terrain under discussion.

S.No. (I)	District (1)	pH (2)	E.C. (3)	HC03 (4)	Cl (5)	NO3 (6)	SO4 (7)	F (8)	Ca (9)	Mg (10)	T.H. (11)	Na (12)	K (13)	SiO2 (14)	d(metre) (15)
1.	Agra	-	5202	805	667	100	730	2.40	28	304	1320	552	5	40	20.3
2.	Allahabad	8.2	662	238	35	53	20	1.70	56	22	230	·12	40	20	4.61
3.	Azamgarh	7.67	3925	842	567	64	350	0.60	116	172	1000	415	63	29	7.27
4.	Banda	-	912	332	74	54	29	0.40	8	40	185	106	30	26	6.79
5.		-	2047	546	309	115	48	0.10	104	64	525	215	1.5	37	10.26 (June)
6.	Bareilly	-	700	329	28	50	380	0.51	88	19	300	29	2.0	40	4.63
7.	Basti	-	4070	903	681	276	169	0.75	112	136	840	530	20	39	6.19
8.	Bijnor	8.3	801	311	85	64	226	0.60	60	41	320	81	1.1	30	8.61
9.	Etawah	7.74	3750	955	20	900	646	2.50	72	83	523	690	6.4	23	3.25
10.	Etah	-	2097	470	298	60	786	2.10	32	75	390	230	101	22	4.20
11.		-	3294	641	496	80	358	2.20	28	61	320	460	150	27	6.30
12.		-	3400	189	447	285	77	0.30	176	164	1115	250	13	19	7.92
13.	Fatehgarh	7.87	6100	1037	113	370	31	1.20	42	462	2005	760	8.0	48	7.50
14.		7.33	3050	578	564	180	358	0.40	138	88	705	500	4.3	34	13.7
15.		7.96	1500	598	170	110	77	0.75	60	70	440	225	2.7	33	3.39
16.		7.74	900	427	57	68	31	0.40	32	33	215	132	4.9	34	12.30
17.	Ghazipur	8.2	2419	464	397	180	120	0.16	276	51	900	154	9	39	110
18.	Gonda	-	1203	366	142	62	65	0.60	36	36	240	96	128	31	2.96
19.		-	104J	329	128	70	28	0.30	68	29	290	101	1.1	31	3.40

TABLE 4.1   Districtwise Chemical Composition Of Ground Water Samples High In Nitrate

S.No. (1)	District (1)	pH (2)	E.C. (3)	HCO3 (4)	Cl (5)	NO3 (6)	SO4 (7)	F (8)	Ca (9)	Mg (10)	T.H. (11)	Na (12)	K (13)	SiO2 (14)	d(metre) (15)
20	Gorakhpur	-	1350	370	206	60	29	0.20	136	78	660	7	9	28	2.73
21	Jhansi	8.2	1888	660	180	170	83	0.80	20	43	225	215	200	22	3.64
22	Kanpur	8.75	1325	522	78	78	60	1.25	16	56	270	235	8.2	32	7.50
23		7.70	1770	561	192	70	62	0.18	116	74	600	116	4.0	-	9.35
24	Lakhanpur	-	2120	732	249	60	134	0.50	104	92	640	200	40	25	5.79
25	Mainpuri	-	2700	833	241	90	169	0.60	40	51	310	299	260	20	4.63
26	Meerut	-	1270	164	142	120	140	0.20	31	55	310	66	84	24	9.09
27	Moradabad	8.6	1557	315	284	180	88	0.45	40	58	340	195	33	30	6.67
28		8.35	1023	366	106	1000	61	1.25	96	60	490	44	2.7	36	10.80 (June)
29	Nainital	-	750	342	21	70	-	0.80	92	29	350	10	10	12	8.75
30		-	2340	646	163	320	105	0.15	132	41	520	105	300	30	2.33
31	Pratapgarh	8.	2176	488	341	80	129	1.40	24	108	505	26	4	32	3.88
32	Saharanpur	-	1250	189	114	140	91	0.06	16	50	250	114	20	35	6.12
33		-	1750	144	270	138	106	0.52	64	82	500	98	2.0	30	7.33
34	Shahjahanpur	-	3050	512	114	150	83	0.18	88	70	510	135	1.7	32	3.50
35		-	900	213	92	80	43	0.20	36	46	280	67	10	30	3.36
36	Unnao	-	2660	854	269	124	182	0.40	128	107	76	760	85	25	5.97
37	Varanasi	7.8	1950	378	266	120	109	0.50	220	75	860	25	3.0	31	16.13
38	Rampur	8.47	1201	340	128	73	104	0.80	32	72	380	90	4.5	30	5.49

TABLE 4.1 Contd. Districtwise Chemical Composition Of Ground Water Samples High In Nitrate

	HCO$_3$	Cl	NO$_3$	SO$_4$	F	Ca	Mg	Na	K	SiO$_2$
HCO$_3$	1.000									
Cl	0.453	1.000								
NO$_3$	0.341	0.281	1.000							
SO$_4$	0.459	0.531	0.524	1.000						
F	0.250	0.268	-0.161	0.363	1.000					
Ca	0.039	0.312	0.297	0.072	-0.430	1.000				
Mg	0.576	0.389	0.522	0.889	0.335	-0.009	1.000			
Na	0.732	0.583	0.447	0.689	0.350	-0.008	0.719	1.000		
K	0.271	0.056	0.243	-0.044	0.101	-0.092	-0.139	0.040	1.000	
SiO$_2$	0.190	0.159	0.308	0.253	0.034	-0.035	0.365	0.313	-0.145	1.000

TABLE 4.2   CORRELATION MATRIX

The negative correlation between nitrate and fluoride in the alluvial plains of U.P. is different from the positive correlation reported by Handa (1975) for groundwater from Rajasthan. It was concluded by Handa that in hard-rock terrains, fluoride level in water is controlled by the dissolution of an accessory mineral like fluorite (CaF_2). In this situation, Ca and F are negatively correlated in order to maintain the solubility product equal to $a_{Ca^{2+}} \times (a_{F^-})^2$.

In the prevailing high pH of groundwater, precipitation of $CaCO_3$ reduces Ca^{2+} concentration and therefore, F^- concentration is relatively high. Application of N-fertilizers and other anthropogenic sources in the same area result in high NO_3^- along with high F. Handa (1975) also mentions that, at relatively low redox potential and in the presence of nitrate reducing bacteria, denitrification is normally accompanied by a rise in pH values. In the U.P. alluvial plains, the positive correlation of NO_3^- with Ca(r=0.297) may indicate simultaneous lowering of Ca and NO_3^- during denitrification in shallow aquifers where Ca is precipitated as $CaCO_3$ (kankar) nodules at relatively high pH. This may also explain the negative correlation between NO_3^- and F^-, provided the source of F^- is dissolution of $Ca-F$ mineral like fluorite or fluor-apatite.

There have been several attempts to correlate NO_3^- with constituents like Cl, Na and K to distinguish the anthropogenic sources. For example, in their study of nitrate pollution of shallow basaltic aquifers, Pawar and Shaikh (1995) concluded that high values of nitrate accompanied by low Cl/NO_3 ratio was strong evidence for fertilizer source of nitrate, whereas high chloride with low nitrate indicated non-fertilizer source like domestic sewage and dissolution of salt crust from soil. Table 4.3 gives the Cl/NO_3 ratios for the present data-base in U.P. alluvial plains.

Here also, high nitrate may point to a N-fertilizer source and high Cl may indicate pollution by domestic sewage or salts.

Das et al.,(1981) found it convenient to use a plot of K/Na mole ratio against nitrate concentration to delineate groundwaters polluted either by K-fertilizers or NO_3^- from fertilizer and sewage. In a general way, highly polluted wells situated near villages or agricultural land had high values of both K/Na mole ratios and NO_3^- concentrations. Figure 4.1 shows such a plot for the data base (ref table 4.1)

It is seen that waters with high K/Na mole ratios are also relatively high in nitrate.

The results of factor analysis are given in Table 4.4 and the same is shown schematically in figure 4.2.

Certain general comments can be made about the factor groupings in terms of the prevailing soil environment,e.g. factor 1 may indicate the association of nitrate derived from anthropogenic sources with constituents of alkaline soils (reh) like Na_2CO_3, Na_2SO_4 and $MgSO_4$ (Wadia,1975). Similarly, factor 2 may represent association with dissolution of CaF_2 as discussed earlier. The relatively high loading of K in factor 3 may indicate limited use of K-fertilizers (Pawar and Shaikh, 1995).

4.3 Redox Reactions

In natural waters, nitrogen exists in various oxidation states.Progressive nitrification consists of several oxidation steps, with NO_3^- as the final product.On the other hand, denitrification consists of reduction of NO_3^- to N_2, through in-

S.No.	NO_3	Cl	Cl/NO_3	S.No.	NO_3	Cl	Cl/NO_3
1	100	667	6.67	20	60	206	3.43
2	53	35	0.66	21	170	188	1.11
3	64	567	3.86	22	78	78	1.00
4	54	74	1.37	23	70	192	2.74
5	115	309	2.69	24	60	249	4.15
6	50	28	0.56	25	90	241	2.68
7	276	681	2.47	26	120	142	1.18
8	64	85	1.33	27	180	284	1.58
9	900	20	0.022	28	1000	106	0.11
10	60	298	4.97	29	70	21	0.30
11	80	496	6.2	30	320	163	0.51
12	285	447	1.56	31	80	341	4.26
13	370	113	0.305	32	140	114	0.81
14	180	564	3.13	33	138	270	1.96
15	110	170	1.55	34	150	114	0.76
16	68	57	0.83	35	80	92	1.15
17	180	397	2.21	36	124	269	2.16
18	62	142	2.29	37	120	266	2.22
19	70	128	1.82	38	73	128	1.75

Table 4.3: Table showing Cl/NO_3 ratios for samples from the data base

Variable	Factor			Communality
	1	2	3	
HCO_3	0.746	-0.076	0.327	0.669
Cl	0.668	0.132	0.138	0.483
NO_3	0.614	0.502	0.165	0.656
SO_4	0.874	-0.018	-0.151	0.787
F	0.385	-.784	0.026	0.761
Ca	0.092	0.842	0.067	0.722
Mg	0.884	-0.056	-0.259	0.851
Na	0.890	-0.096	0.027	0.802
K	0.077	-0.090	0.903	0.829
SiO_2	0.413	0.101	-0.452	0.384
Percentage of variance explained by factor	40.5	16.3	12.7	
Cumulative percentage of variance	40.5	56.8	69.5	

Table 4.4: R-mode varimax factor matrix of chemical data for groundwater samples from the alluvial plains of U.P.

termediate species like NO_2^-, NH_3, NH_4^+. Therefore, nitrification-denitrification reactions which control the occurrence of nitrate in water can be interpreted in terms of :

(a) partial pressure of O_2 gas and/or

(b) Eh-pH relations.

4.3.1 Oxygen Pressure

Table 4.5 lists the reactions between the selected dissolved species NO_3^-, NO_2^-, NH_3 and NH_4^+ in terms of partial pressure of oxygen (P_{O_2}). The equilibrium constant (K) can be calculated from the equation :

$$\Delta G_r^0 = -RT \ln K \qquad (4.1)$$

where ΔG_r^0 is the change in Gibbs energy during reaction under standard conditions. For this purpose, the relevant Gibbs energy of formation (ΔG_f^0) values are listed in Table 4.6. Using these values, the expressions for $\log P_{O_2}$ have also been listed in Table 4.5. The linear equations have been plotted in the $\log P_{O_2}$-pH graph in figure 4.3. A sample calculation is given below:
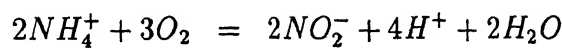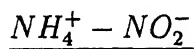
$$\underline{NH_4^+ - NO_2^-}$$

$$2NH_4^+ + 3O_2 = 2NO_2^- + 4H^+ + 2H_2O$$

$$\Delta G_r^0 = [2(\Delta G_r^0)_{NO_2^-} + 4(\Delta G_r^0)_{H^+} + 2(\Delta G_r^0)_{H_2O}]$$
$$- [2(\Delta G_r^0)_{NH_4^+} + 3(\Delta G_r^0)_{O_2}]$$

1. $NO_2^- - NO_3^-$	$: 2NO_2^- + O_2 = 2NO_3^-$
	$\log P_{O_2} = -26.01$
	$for\ a_{NO_2^-} = a_{NO_3^-}$
2. $NH_4^+ - NO_2^-$	$: 2NH_4^+ + 3O_2 = 2NO_2^- + 4H^+ + 2H_2O$
	$\log P_{O_2} = -22.5 - 1.33pH$
	$for\ a_{NH_4^+} = a_{NO_2^-}$
3. $NH_4^+ - NO_3^-$	$: 2NH_4^+ + 4O_2 = 2NO_3^- + 4H^+ + 2H_2O$
	$\log P_{O_2} = -23.35 - pH$
	$for\ a_{NH_4^+} = a_{NO_3^-}$
4. $NH_3 - NO_2^-$	$: 2NH_3 + 3O_2 = 2NO_2^- + 2H^+ + 2H_2O$
	$\log P_{O_2} = -28.64 - 0.67pH$
	$for\ a_{NH_3} = a_{NO_2^-}$
5. $NH_4^+ - NH_3$	$: NH_4^+ = NH_3 + H^+$
	$pH = 9.25$
	$for\ a_{NH_4^+} = a_{NH_3}$

Table 4.5: Reactions between selected dissolved nitrogen species NO_3^-, NO_2^- and NH_4^+ in terms of $\log P_{O_2}$ and pH.

	Valency of N	ΔG_f^0(kJ/mol)	Source
O_2		0	b
H^+		0	b
NO_2^-	+3	-34.52	a
NO_3^-	+5	-108.74	b
NH_4^+	-3	-79.31	b
H_2O		-237.13	b

Table 4.6: Gibbs Energy Values for Redox Reactions.
Note :a = original value from Garrels and Christ,converted to kJ/mol,b = value from Drever, 1988

$$\Delta G_r^0 = -384.68 \ kJ$$

$$K = \frac{(a_{NO_2^-})^2 \times (a_{H+})^4}{(a_{NH_4^+})^2 \times (P_{O_2})^3}$$

$$\log K = -3 \log P_{O_2} - 4pH$$

$$and \ \log K = -\frac{\Delta G_r^0}{5.707} = -\frac{-384.68}{5.707} = 67.4$$

$$\log P_{O_2} = -22.5 - 1.33pH$$

It is seen that undissociated NH_3 is dominant at pH higher than 9.25. In the intermediate pH range of 6 to 8, which is relevant for most natural waters, NO_3^- is dominant at P_{O_2} higher than 10^{-26} atm. The P_{O_2} for $NO_2^- - NH_4^+$ equilibrium decreases with increasing pH. NH_4^+ is dominant at relatively low P_{O_2}.

4.3.2 Eh–pH relationships

An increase in the oxidation state of nitrogen can also be represented by an oxidation half-cell which has the general form:

Reduced species = Oxidized spcies + $n\bar{e}$ (Raymahashay,1996)

The transfer of electrons in such reactions generates a redox potential, which can be defined by the Nernst Equation:

$$
\begin{aligned}
Eh &= E^0 + \frac{RT}{nF}ln(\frac{Ox}{Red}) \\
&= E^0 + \frac{2.303\,RT}{nF}\log(\frac{Ox}{Red})
\end{aligned}
$$

$where\ Eh\ =\ redox\ potential\ measured\ with\ reference$

$to\ the\ hydrogen\ half\ cell, H_2 = 2H^+ + n\bar{e}$

$E^0\ =\ standard\ potential\ i.e.\ redox\ potential\ for\ the$

$reaction\ at\ 25^0\ C\ with\ all\ substances\ at\ unit\ activity.$

$R\ =\ Gas\ law\ constant\ =\ 8.314 \times 10^{-3}\ kJ/deg - mol.$

$T\ =\ Temperature\ in\ ^0K.$

$n\ =\ number\ of\ electrons\ released.$

$F\ =\ 96.48\ kJ/v - g.equivalent$

$\frac{Ox}{Red}\ =\ Reaction\ quotient\ giving\ appropriate\ activity\ ratio$

$of\ oxidized\ to\ reduced\ species.$

E^0 is related to the change in Gibbs energy during the oxidation reaction under standard conditions(ΔG_r^0).

$$
E^0 = \frac{\Delta G_r^0}{nF} \tag{4.2}
$$

In many electrochemistry texts, redox reactions are represented by a reduction half-cell :

$$Oxidized\ species + n\overline{e} = Reduced\ species \qquad (4.3)$$

In this case,

$$Eh = E^0 - \frac{RT}{nF} ln(\frac{Red}{Ox}) \qquad (4.4)$$

and

$$E^0 = -\frac{\Delta G_r^0}{nF} \qquad (4.5)$$

where ΔG_r^0 is the change in Gibbs energy during reduction reaction under standard conditions. However the final expression remains unchanged because

$$ln(\frac{Red}{Ox}) = -ln(\frac{Ox}{Red}) \qquad (4.6)$$

and $(\Delta G_r^0)_{reduction} = -(\Delta G_r^0)_{oxidation}$.

For reactions involving H^+ ion, pH becomes a variable in the Nernst equation as seen in the expressions listed in table 4.7, which is based on the ΔG_r^0 values in table 4.6.

A sample calculation is shown below :

$\underline{NH_4^+ - NO_2^-}$

$$NH_4^+ + \frac{3}{2}O_2 = 2H^+ + NO_2^- + H_2O$$

$$3H_2O = 6H^+ + \frac{3}{2}O_2 + 6\overline{e}$$
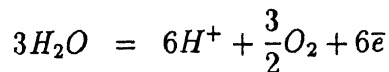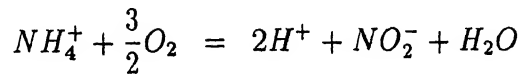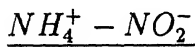
$1. NH_4^+ - NO2^-$	:	$NH_4^+ + 2H_2O = NO_2^- + 8H^+ + 6\bar{e}$
		$Eh = 0.896 - 0.079 pH$
		for $a_{NH_4^+} = a_{NO_2^-}$
$2. NO_2^- - NO_3^-$	:	$2NO_2^- + 2H_2O = 2NO_3^- + 4H^+ + 4\bar{e}$
		$Eh = 0.844 - 0.059 pH$
		for $a_{NO_2^-} = a_{NO_3^-}$
$3. NH_4^+ - NO_3^-$	:	$NH_4^+ + 3H_2O = NO_3^- + 10H^+ + 8\bar{e}$
		$Eh = 0.883 - 0.074 pH$
		for $a_{NH4^+} = a_{NO_3^-}$
$4. NH_4^+ - NH_3$	:	$NH_4^+ = NH_3 + H^+$
		$pH = 9.25$ for $a_{NH_4^+ = a_{NH_3}}$
$5. NH_3 - NO_2^-$	:	$NH_3 + 2H_2O = NO_2^- + NO_2^- + 7H^+ + 6\bar{e}$
		$Eh = 0.805 - 0.07 pH$
		for $a_{NH_3} = a_{NO_2^-}$

Table 4.7: Reactions between selected dissolved N species in terms of Eh and pH

$$NH_4^+ + 2H_2O = 8H^+ + NO_2^- + 6\bar{e}$$
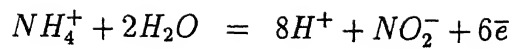
$$\Delta G_r^0 = [(\Delta G_r^0)_{NO_2^-} + 8(\Delta G_r^0)_{H+} + 6(\Delta G_r^0)_{\bar{e}}]$$

$$-[(\Delta G_r^0)_{NH_4^+} + 2(\Delta G_r^0)_{H_2O}]$$

$$\Delta G_r^0 = 519.05 \; kJ$$

Substituting the values in

$$Eh = E^0 + \frac{RT}{nF} 2.303 \log \frac{Ox}{Red} \; where \; E^0 = \frac{\Delta G_r^0}{nF}$$

$$Eh = 0.896 + 0.632 \log \frac{a_{NO_2^-} \times (a_{H+})^8}{a_{NH_4^+}}$$

$$Eh = 0.896 - 0.079 pH \; for \; a_{NH_4^+} = a_{NO_2^-}$$

The linear equations obtained by this method have been plotted on the Eh-pH diagram shown in figure 4.4. The Eh-pH ranges of river and groundwater (Garrels and Christ, 1965) are also shown on the diagram. It is seen that NO_3^- is the main dissolved species at high Eh values. NO_2^- has a narrow field of stability below $Eh = 0.69 \, v$ and pH above 2.6. Undissociated NH_3 is dominant under low Eh-high pH conditions whereas NH_4^+ ion is the main species at low Eh and pH below 9.25. This diagram also indicates that aerated river waters will be dominated by NO_3^- whereas in ground water at low Eh values, NO_3^- will be reduced to NH_4^+.

As shown in table 4.7, the Eh-pH equations are dependent on the ratio between oxidized and reduced species. For example, in figure 4.5, a part of fig. 4.4 has been enlarged to depict the $NO_3^- - NO_2^-$ boundary at different NO_3/NO_2^- mole ratios. Such a diagram is useful to predict the Eh value if m_{NO_3}/m_{NO_2} and pH are known. To illustrate this application, relevant information on the Pandu river near IIT Kanpur has been listed in table 4.8. From the position of the river water

S.No.	pH	m_{NO_2} (mg/L)	m_{NO_3} (mg/L)	$\frac{m_{NO_3}}{m_{NO_2}}$	Calculated Eh (v)
1	8.5	1.08	1.40	0.96	0.342
2	8.4	0.92	1.55	1.25	0.351
3	8.3	0.90	1.85	1.71	0.361
4	8.43	0.57	1.35	1.75	0.353
5	8.11	0.50	1.35	2.0	0.374
6	8.2	0.475	1.70	2.65	0.372
7	7.8	0.35	1.90	4.02	0.401

Table 4.8: Eh values calculated from pH, nitrite and nitrate in Pandu river. Original data from Srivastava (1972).

analysis on figure 4.5, the Eh values have been calculated in the last column of table 4.8. It is interesting to note that the calculated Eh values fall in the range suggested by Garrels and Christ (1965) for river waters.

4.4 Nitrate-Depth Relationship

From the depth to water-table listed in the original data base (table 4.1), four subsets were created according to the trend of increase or decrease of NO_3^- with depth. These are graphically displayed in figures 4.6 to 4.9. It is interesting to note that increasing trends are present in depths ranging from (i)0 to 5 m and (ii)0 to 10 m. In contrast, decreasing trends are seen from (iii)0 to 15 m and (iv)0 to 25 m. In other words, the nitrate concentration increases with the depth of water table when the saturation zone is relatively shallow, i.e. around 10 m. Moreover, the slope of the regression line (hence the rate of increase of NO_3^- with depth) is higher for the shallowest aquifer upto 5 m. This trend in alluvial terrain

matches with the data supplied by Pawar and Shaikh (1995) from the Deccan Trap Hydrologic Province (figure 4.10). In both situations, it can be concluded that biological denitrification reactions are predominant in organic-rich shallow depths, whereas at deeper levels, lack of denitrification results in an increase in NO_3^- concentrations.

When depths of the order of 15 to 25 m are considered, the influence of aquifer mineralogy apparently overcomes biological reduction. In several deep aquifers, a sharp redox boundary (redoxcline) has been postulated which subdivides the aquifer into an upper 10-15 m oxic zone where NO_3^- level is high in the presence of O_2 i.e. at high Eh, and a lower anoxic zone characterized by Fe^{2+} rich waters where oxidation of Fe^{2+} is accompanied by a reduction of NO_3^- (Edmunds and Walton, 1983; Pedersen et al.,1991; Postma and Boesen, 1991). In the present data from the alluvial terrain of U.P.,the transition from increasing trend to decreasing trend of NO_3^- with depth once again lies between 10-15 m. Therefore, a redoxcline at this depth range can be suggested for these aquifers. If a redoxcline exists at some depth in an aquifer, it is anticipated that there will be a marked difference between the nitrate content of shallow dug-wells and relatively deeper tube-wells. The data from the Nagaur district of Rajasthan (Gupta, 1992) show that tube-well waters have significantly lower nitrate concentration compared with dug-well water samples. A similar trend in an unconfined sandy aquifer was explained by Postma and Boesen (1991) in terms of reduction of nitrate by pyrite at depth below the redoxcline.

An attempt was made to compare nitrate levels in dug-wells and deep-wells around IIT-K campus. Nitrate concentrations determined by the UV spectropho-

No.	Location	Type of well	Depth (m)	NO_3 ppm
1	IIT Gate	Dug-well	11.2^a	Below detection
2	Devi Sahay Nagar	Dug-well	11.0^a	3.05
3	Nankari	Dugwell	8.0^a	36.5
4	Barasirohi	Dug-well	1.9^a	5.65
5	IIT Gate	Tube-well	36.6^b	Below detection
6	Devi Sahay Nagar	Tube-well	36.6^b	19.8
7	Nankari	Tube-well	33.5^b	27
8	Barasirohi	Tube-well	24.4^b	11.5

Table 4.9: Dug-well and Tube-well samples around IIT-K
pH of dug-well samples = 7.3 to 7.6
pH of tube-well samples = 6.8 to 7.0 at $t = 10^0 C$
Date of sampling : November, 1995.
a: measured, b: reported by local residents

tometric method described in chapter three are presented in table 4.9. The same data have been plotted in figure 4.11. The number of samples is too less to decipher a definite trend. However, considering the high nitrate waters, the tube wells (No. 6,7,8) have lower values compared to the dug-well (No. 3) which appears to be heavily polluted by domestic sewage. The depth of these tube-wells is greater than the redoxcline suggested at 10-15 m from the CGWB data base. On the other hand, shallow dug-wells 1,2 and 4 indicate partial denitrification by organic matter above the redoxcline.

4.5　Comparison with Deccan Trap Hydrologic Province

As mentioned earlier, a detailed description of the occurrence of NO_3^- in groundwater in Deccan basalt has appeared recently in the literature (Pawar and Shaikh, 1995). Some major differences have been observed in the soil and water quality factors when compared with the present investigation in the alluvial plains of Uttar Pradesh. These have been summarized below.

To start with, the nature of weathering and soil formation is different in the two regions. The soil profile over Deccan basalt can be classified as the *residual type*. The constituent minerals in bedrock undergo chemical weathering in situ and there exists a close relationship between the mineralogy of the soil and the bedrock. For example, olivine, pyroxene, and Ca-plagioclase readily weather into a montmorillonite (smectite) type of clay mineral under moderate rainfall and at poorly drained foothills (Lunkad and Raymahashay, 1978; Karale, 1984). This is because appreciable amounts of released ions (bases) are retained in the weathering complex under mild leaching conditions. This mineral is the major constituent of expansive black cotton soil. On the other hand, in heavy rainfall regions and well-drainedslopes, Ca^{2+}, Mg^{2+} and SiO_2 are rapidly leached from the clay mineral lattice. The residual soil is enriched in insoluble Fe^{3+}-hydoxides and a lateritic profile develops. Table 4.10 gives the average chemical composition of Deccan basalt. Depth-wise chemical analyses of a black cotton soil profile are given in table 4.11.

The basaltic flows constitute a multi-aquifer system separated by thin impervious layers of red and black soil. Ground water occurs mainly in the joints, vesicles and fissures in massive basalt and in the contact between lava flows. Large diameter

Sio_2	50.61
Al_2O_3	13.58
Fe_2O_3	3.19
FeO	9.92
MnO	0.16
MgO	5.46
CaO	9.45
Na_2O	2.60
K_2	0.72
TiO_2	1.91

Table 4.10: Mean chemical composition (%) of the Deccan Traps.
Source : Krishnan (1960)

dug-wells penetrate the soil cover and local patches of alluvium. The wells studied by Pawar and Shaikh (1995) have a depth range of between 0.76-9.1 m; the nitrate ranging from 2.2 mg/L to 64 mg/L is mainly derived from agricultural land where excessive amounts of N-fertilizers have been applied. It is apparent that in these aquifers biological denitrification is more effective at shallow depths. The concentration of nitrate increases with depth mainly because of the lack of organic matter. The soil mineralogy indicates that oxidizable Fe^{2+}-minerals are also not available for reduction of NO_3^-.

Table 4.12 compares black soil profile over basalt with the typical subsurface lithology in Gangetic alluvium. This alluvium is an enormous thickness of sediments which filled the Indo-Gangetic trough created in front of the rising Himalayas (Krishnan, 1960). A deep granitic basement is successively overlain by

Depth (m)	pH	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO
0-35	6.5	39.49	30.23	23.31	1.88	1.93
35-63	6.6	39.74	22.24	32.16	1.43	1.49
63-90	5.9	40.73	27.55	25.45	1.14	1.14
90-120	6.1	40.65	24.32	28.26	1.51	1.74
120-150	6.0	42.19	25.39	16.87	1.24	1.40
150-180	6.0	42.69	23.46	24.18	1.34	1.38

Table 4.11: Analytical data of typical basaltic profile under heavy rainfall conditions. From Karale (1984).

Vindhyans, Tertiary Sediments and Quaternary Sediments. The Quaternary sediments which form the main reservoir of groundwater are a sequence of channel fill and flood plain deposits of a large river system i.e. the Ganga and its tributaries. As seen in table 4.12, the main aquifers are sand layers alternating with kankar rich silt/clay layers. There are occasional perched aquifers within thick back swamp clay horizons. In the IITK area, the aquifers contain subrounded and dominantly iron-stained quartz grains with some feldspar and mica. The heavy minerals found are pink garnet, zircon, tourmaline and hornblende (Gokhale, 1971).

Because of the high density of population, the source of NO_3^- in ground water has to be domestic sewage along with N-fertilizers. As mentioned earlier, high levels of nitrate are found in dug-wells near villages. In contrast with the basaltic terrain, deeper dug-wells and tube-wells show a decreasing trend. This may be due to lesser nitrate pollution at depth and denitrification by iron minerals like hornblende and garnet which,like pyrite, act as electron donors for reduction of

Gangetic Alluvium		Soil over basalt	
Depth(m)	Description	Depth(m)	Description
0-14	Clay / silt with kankar nodules	0-0.05	Dark, clayey soil with lime concretions and roots.Sticky and plastic
14-24	Sand.		
24-26	Clay / silt with kankar nodules	0.05-0.39	Very dark clay with few lime concretions and roots. Sticky and plastic.
26-28	Sand.		
28-38	Clay / silt with kankar nodules	0.39-0.98	Very dark clay with few roots. Sticky and plastic
38-46	Sand.		
46-60	Clay / silt with kankar nodules	0.98-1.10	Very dark clay. Sticky and plastic.
60-64	Sand.		
64-79	Clay / silt with kankar nodules	1.10+	Weathered basalt
79-87	Sand.	Base not seen	Basalt.
87-107	Clay / silt with kankar nodules		

Table 4.12: Comparison of soil profiles from Gangetic Alluvium and Basalt
Original data from Bisaria and Roy (1976) and Rao and Krishna Murti (1984)

nitrate.

4.6   Comparison with phosphate adsorption by lateritic soils

Both nitrate and phosphate play important roles in eutrophication of polluted waters. While phosphate fixation by soil is a well established process, it is commonly observed that NO_3^- ion moves unhindered through soils. The only mechanism for inorganic nitrogen removal in soil is by fixation of NH_4^+ ion.

Phosphate is fixed on soil clay minerals by anion exchange as well as by formation of insoluble Fe, Al hydroxy-phosphate compounds (Brady, 1990). This has been confirmed by previous experimental work where among various soil types, lateritic soils containing positively charged ferric hydroxide colloids have been shown to be most efficient for phosphate uptake(Mehta,1982).

In order to confirm that similar conditions do not help in removal of nitrate (which is also an anion), similar experiments were repeated with nitrate instead of phosphate in solution. The experimental details are given in chapter three. The results have been summarized in table 4.13.

In 1% suspension of lateritic soil from Calicut, Kerala 88.6% phosphate was removed in 24 hours from an initial concentration of 10 mg/L. The same soil removed only 5% NO_3^- under identical conditions of soil : solution ratio, initial concentration and reaction time. The temperature of the nitrate experiment was, of course, lower. In order to avoid error due to low concentration, data were compared for higher initial concentrations.With initial concentration of 25 mg/L, 76% phosphate had been removed in 24 hours by Mehta (1982) whereas

Type of lateritic soil suspension	Reaction time (hrs)	Initial conc. (ppm)	Temp (deg C)	Initial pH	Final pH	Final conc. (ppm)	Percent removed
* 0.5 g soil in 50 ml PO_4 soln (1 percent)	24 24	10 25	27 28	5.1 4.9	6.6 5.6	1.14 6.00	88.6 76.0
0.5 g soil in 50 ml NO_3 soln. (1 percent)	24 24 76	10 20 20	14 17 15	6.8 6.9 6.8	6.9 6.4 6.8	9.5 16.65 19.35	5.0 16.75(?) 3.25
1 g soil in 50 ml NO_3 soln (2 percent)	24	20	17	6.9	6.4	18.15	9.25

* Data taken from Mehta (1982)

Table 4.13: Results of adsorption experiment

from an initial concentration of 20 mg/L, only 3.25% nitrate was removed even after a longer reaction time of 76 hours during the present experiment. There was only marginal increase in nitrate removal by increasing the strength of the soil suspension. For example, in a 2% soil suspension, 9.25% was removed from 20 mg/L nitrate solution in 24 hours. As indicated in table 4.13, nitrate removal in 1% suspension from 20 mg/L initial concentration after 24 hours gave an ambiguous high value of 16.75%.

Taking an overall view of these experimental results, it is clear that unlike phosphate adsorption, lateritic soil is not able to remove nitrate from initial con-

centration in the 10-20 mg/L range. As removal decreases with higher initial concentration for both PO_4^{3-} and NO_3^-, this would not be an effective mechanism for attenuating the dispersion of pollution derived nitrate in aquifers.

In fact, a review of the coordination chemistry of PO_4^{3-} and NO_3^- ions indicates that in spite of both being anions, the ionic charge, molecular structure and ligand strength makes phosphate more efficient in forming insoluble complexes with charged clay and $Fe(OH)_3$ colloids in the soil environment. The difference in behaviour of phosphate and nitrate can be explained with the help of :

- Structure of ion : The phosphate ion has a tetrahedral structure, while the nitrate ion has a planar structure as shown in the figure 4.12.

- Charge of ion : The phosphate ion has charge -3, while the nitrate ion has a charge of -1, which indicates that phosphate can get more readily fixed on the positive sites on clays and iron oxide colloids present in laterite as compared to nitrate.

- Ligand strength : NO_3^- is a weak ligand as shown in the spectrochemical series, which explains why it does not form any bond with the positive sites present on clay molecules.

- Lewis structure : The Lewis structures of nitrate and phosphate are as shown in the figure 4.13 The formal charge on phosphorus is 0, whereas that on nitrogen is +1. The nitrogen in the nitrate ion therefore attracts the electrons of oxygen atoms towards itself,making the electrons less readily available for bonding with the positively charged ions of clay.

4.7 Summary

Different approaches were taken to interpret the occurrence of nitrate in ground water in U.P. alluvial plains. These results added to the existing CGWB data base. In a terrain like the U.P. alluvial plains with intensive cultivation and high population density, NO_3^- in ground water can be acquired from N-fertilizers as well as from domestic wastewater. Out of N (urea),P (phosphate) and K (KCl) fertilizers, the use of N-fertilizers is of the order of 62% (Lunkad, 1994). This is a major source of nitrate after nitrification. P and K fertilizers can also provide appropriate nutrient balance for nitrifying organisms (Brady, 1975). In ground water the nitrate acquired from these sources coexists with other constituents derived from dissolution of rock/soil forming minerals and saline patches in soil. As illustrated by the statistical analysis of the CGWB data base, this gave low positive correlation coefficients between nitrate and other ions. A negative correlation with F can be explained by CaF_2 dissolution and simultaneous precipitation of $CaCO_3$ (kankar nodules) at high pH caused by denitrification at low Eh values. High Cl concentrations in waters with low NO_3^- may indicate non-fertilizer source like domestic wastewater.

A major feature of nitrate occurrence is a contrasting relationship with depth in aquifers with shallow depth to water table when compared with deeper water table situations. In the first case, lower nitrate values occur near the top of the aquifers due to several factors including accumulation of soil organic matter, abundance of denitrifying bacteria, higher levels of dissolved organic matter and anaerobic conditions in water filled pore spaces(Hiscock

et al.,1991; Pawar and Shaikh,1995).When the water table is deeper, an opposite trend of decreasing NO_3^- with increasing depth can be deciphered. This is explained by the role of Fe^{2+} bearing minerals as electron donors which favours non-microbial NO_3 reduction. The transition depth separating the biological denitrification from the mineralogical denitrification occurs at about 10 m, similar to the redoxcline described by Postma and Boesen (1991).

A limited number of samples collected from the IITK area also showed that tube-well waters had lower nitrate concentrations compared to dug-well situated within a village.

In order to confirm that the NO_3^- ion behaves differently from the PO_4^{3-} anion with respect to adsorption by soil clay minerals and iron hydroxide colloids, experiments were conducted with lateritic soil from Kerala which had shown high phosphate uptake. The lack of NO_3^- adsorption was explained in terms of the molecular structure.

Figure 4.1

Plot of Nitrate vs K/Na mole ratios.
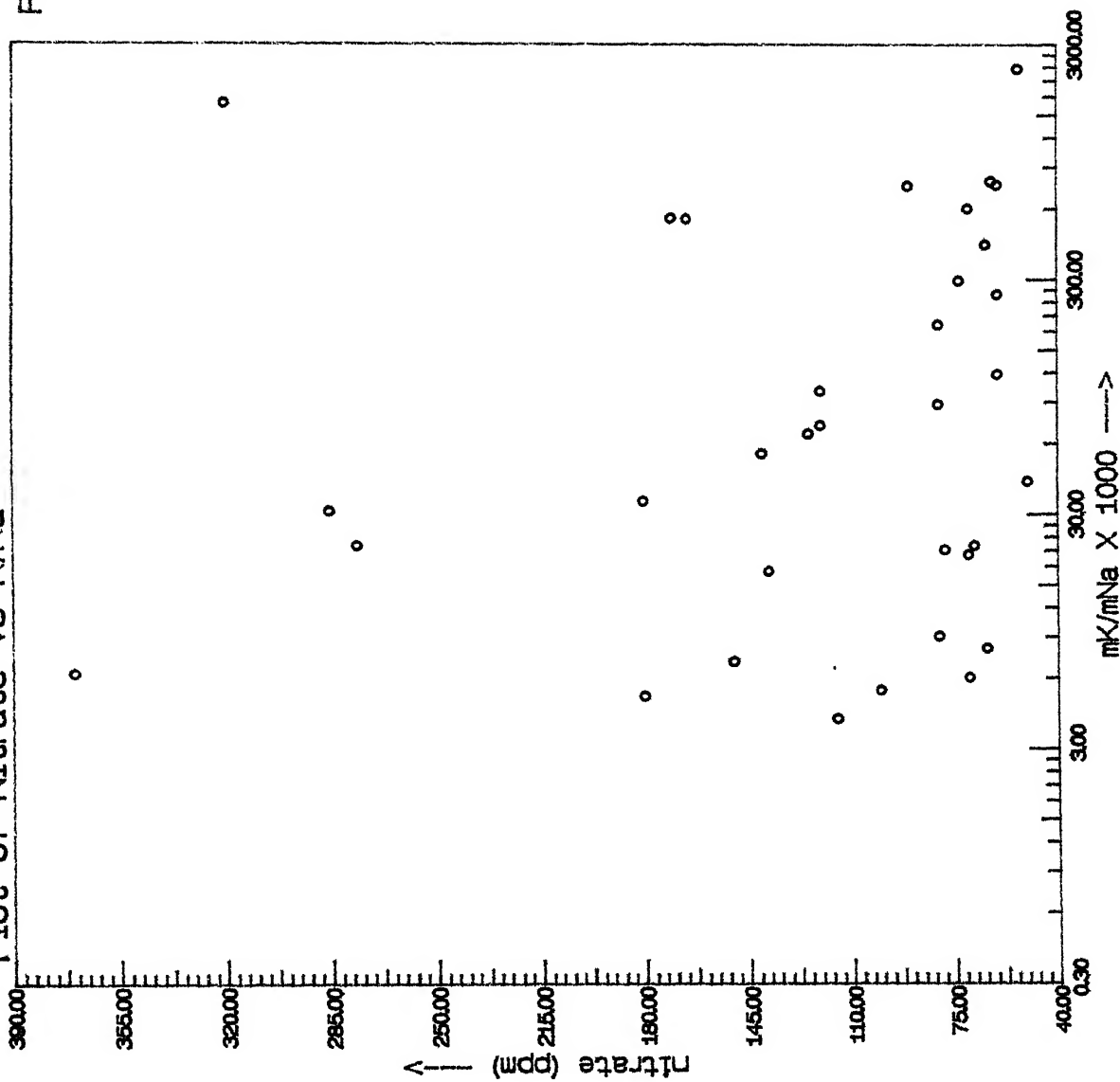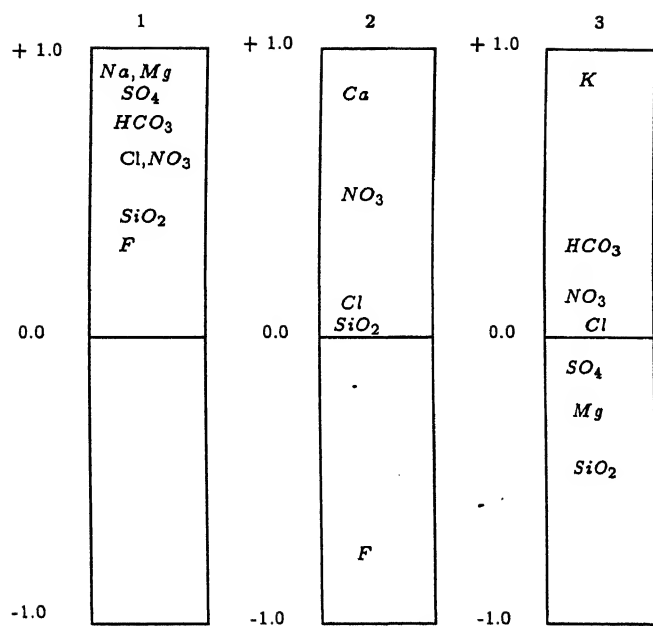
Figure 4.2: Schematic representation of factors from R-mode varimax solution of chemical data for groundwater samples from the alluvial   plains of U.P.
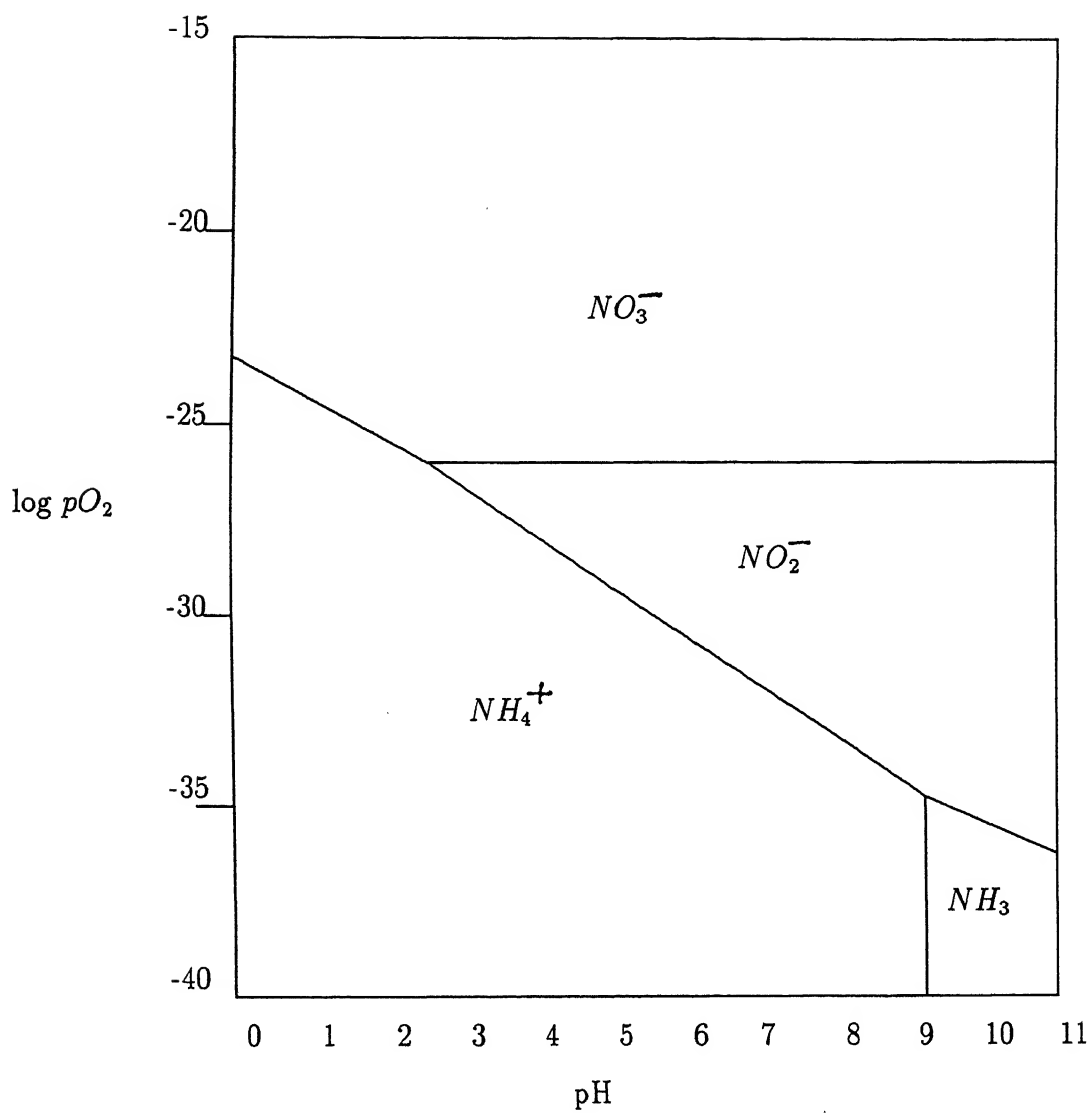
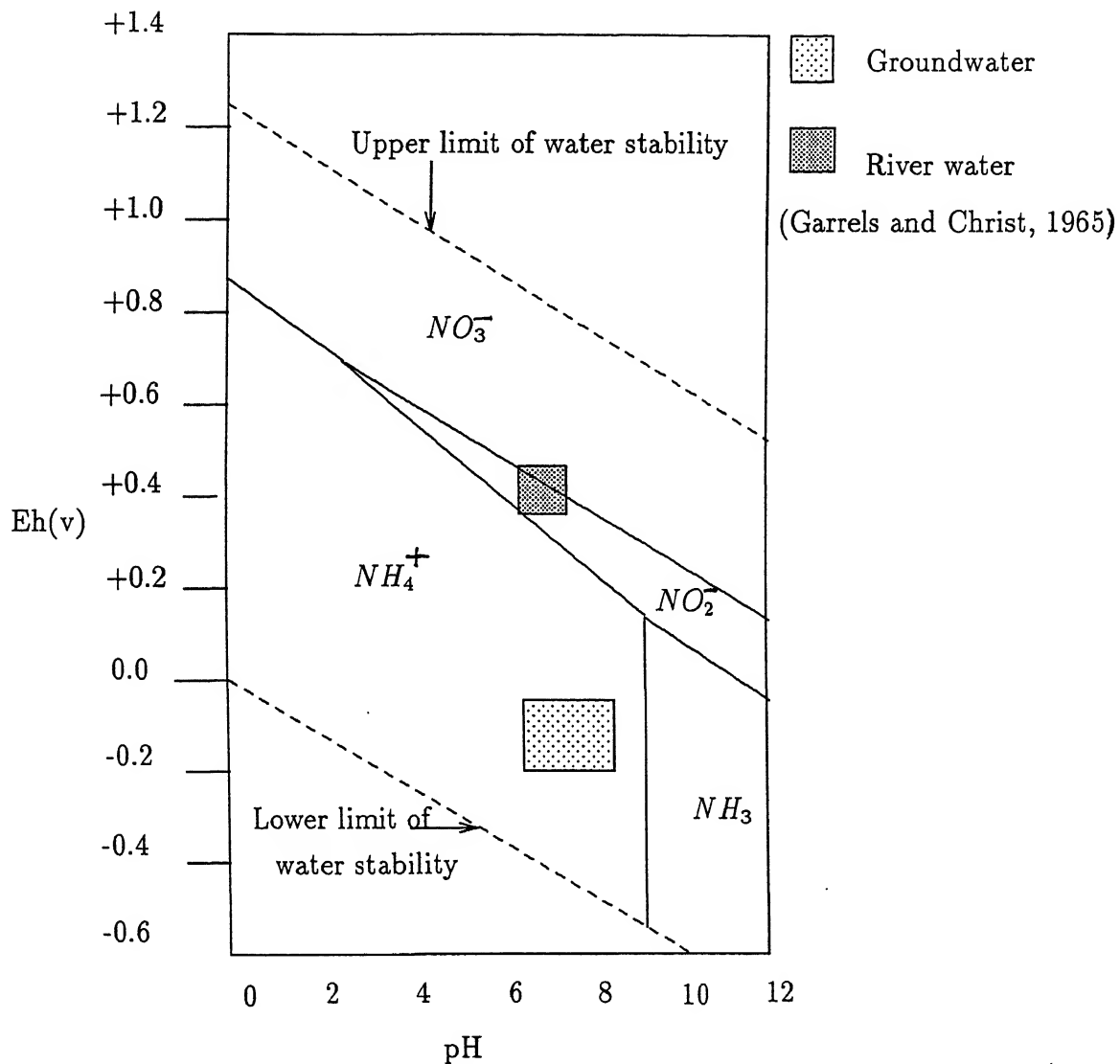Figure 4.3: Oxygen Pressure Diagram for Selected Dissolved Nitrogen Species

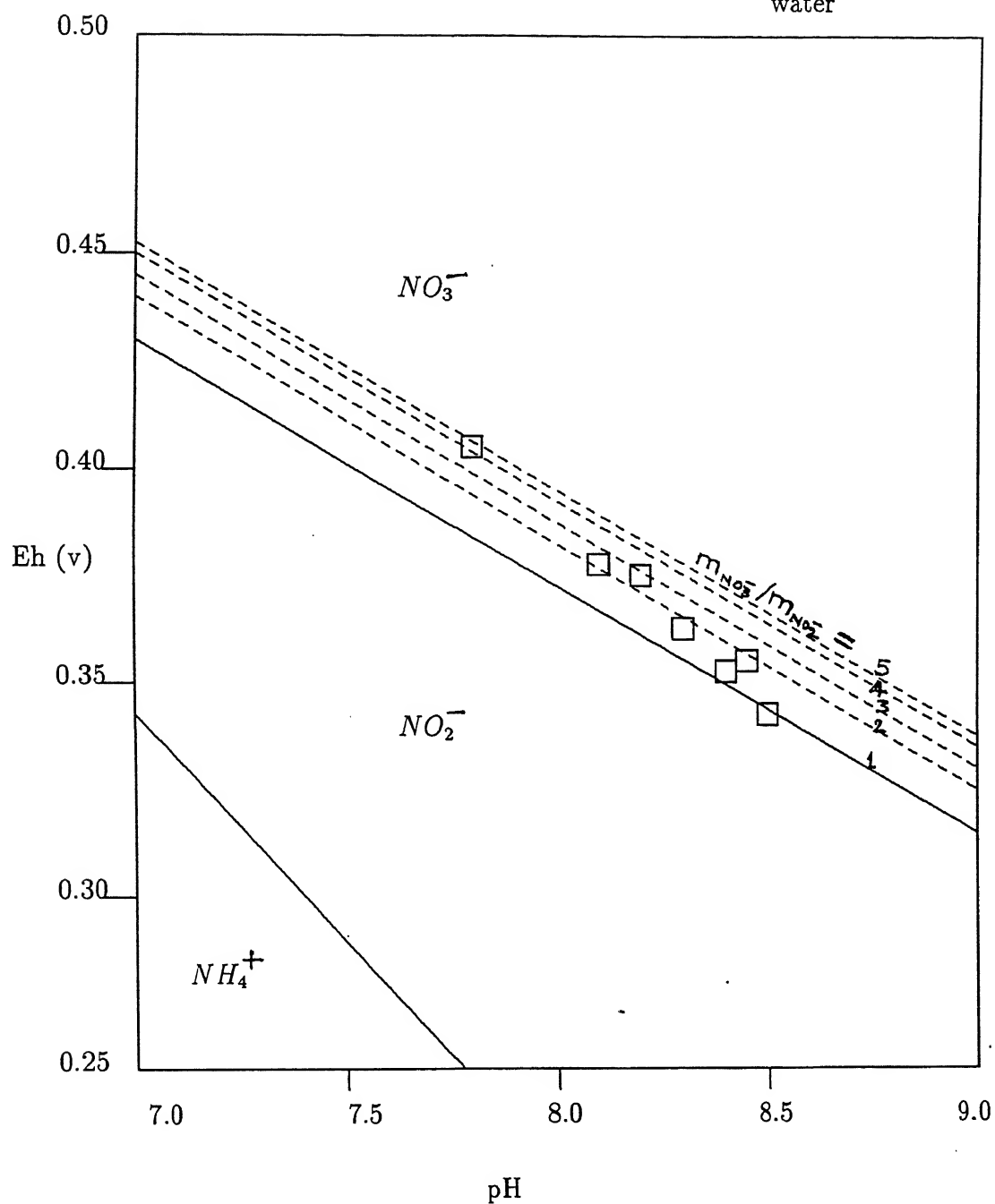Figure 4.4: Eh-pH Diagram for Selected Dissolved Nitrogen Species

Figure 4.5: $NO_3^- - NO_2^-$ Boundaries at different NO_3^-/NO_2^- mole ratios

Figure 4.6

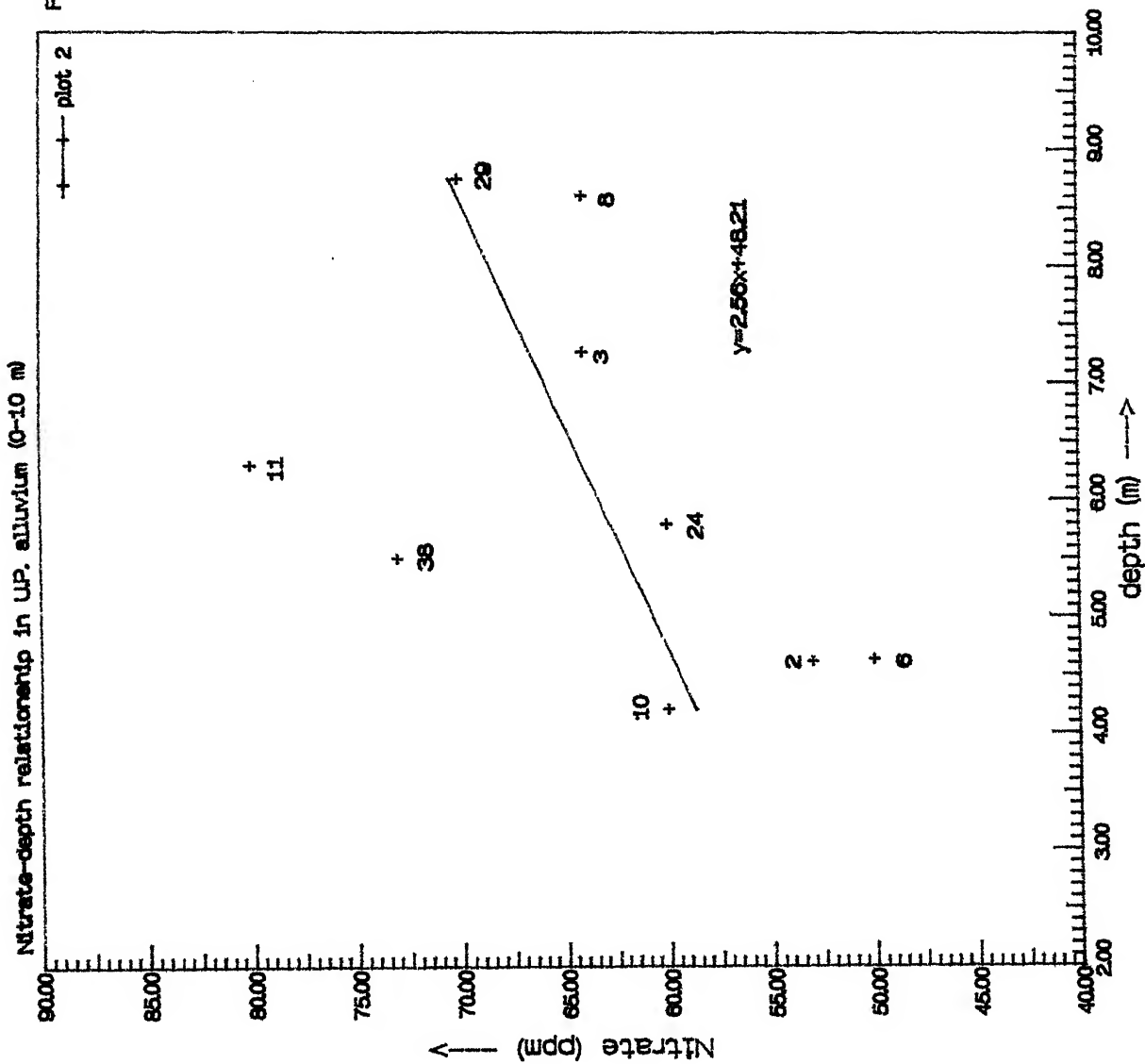Nitrate-depth relationship in U.P. alluvium. (0-5 m)
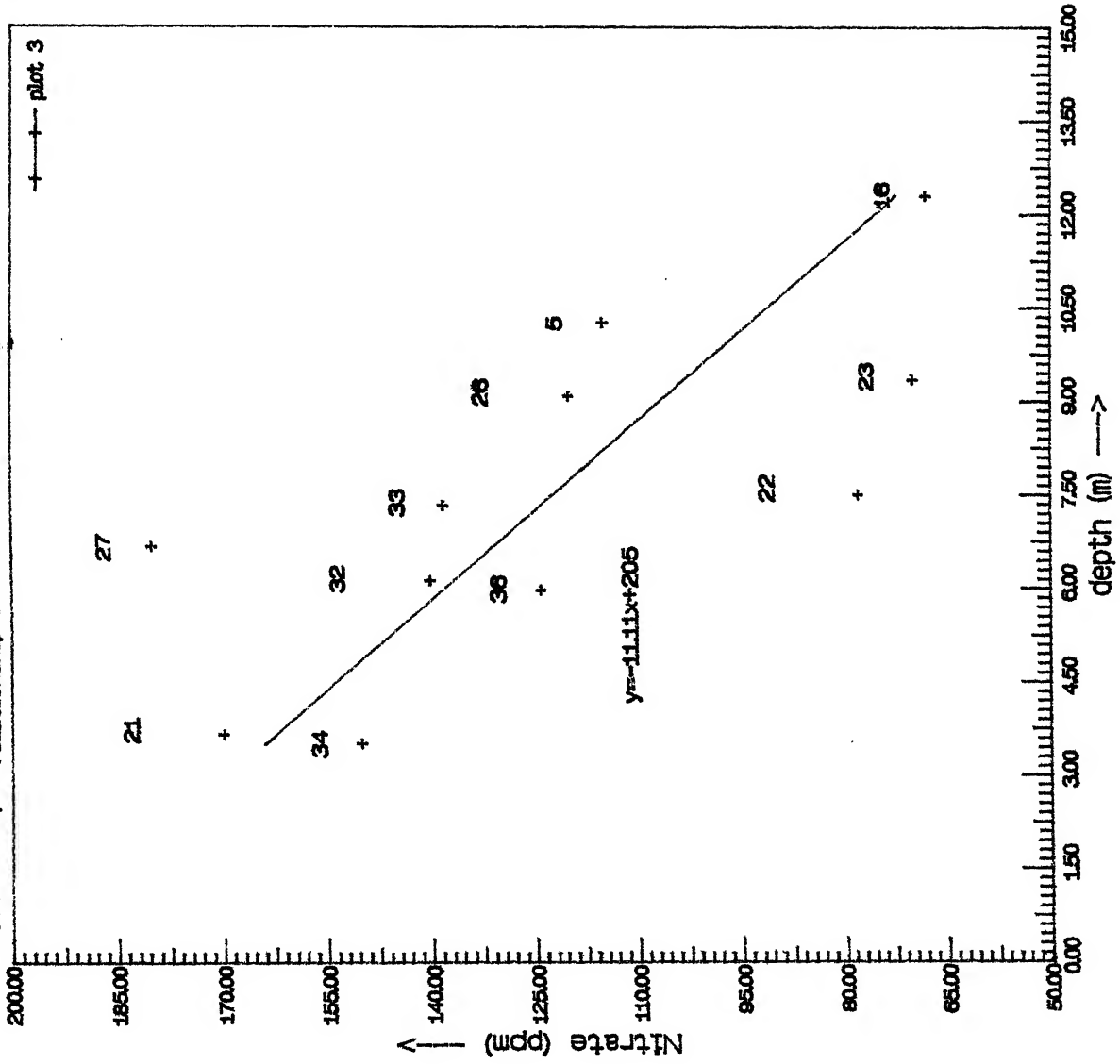
y=16.67x+16.65

depth (m) ----->

Nitrate (ppm) ----->

+ —— plot 1

UsPlot

1 4 3.200000
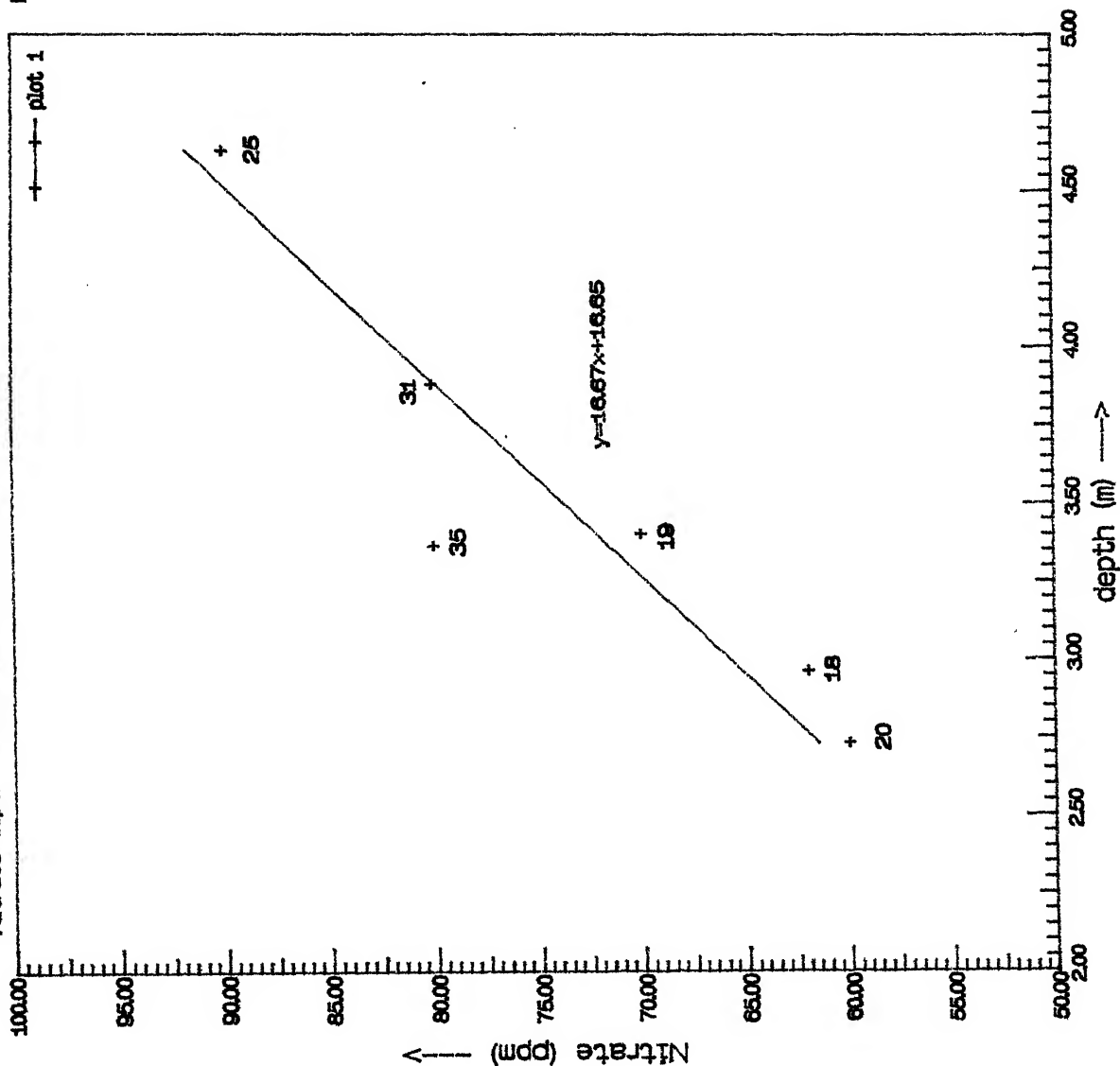
Figure 4.7

Nitrate-depth relationship in U.P. alluvium (0-10 m)

$y=2.56x+48.21$

+—+— plot 2

depth (m) —>

Nitrate (ppm) —>

UsPlot

swati * cs-iit/k : tejas * 03/09/98 12:50:42 *

Figure 4.8

Nitrate-depth relationship in U.P. alluvium (0-15 m)

$y=-11.11x+205$
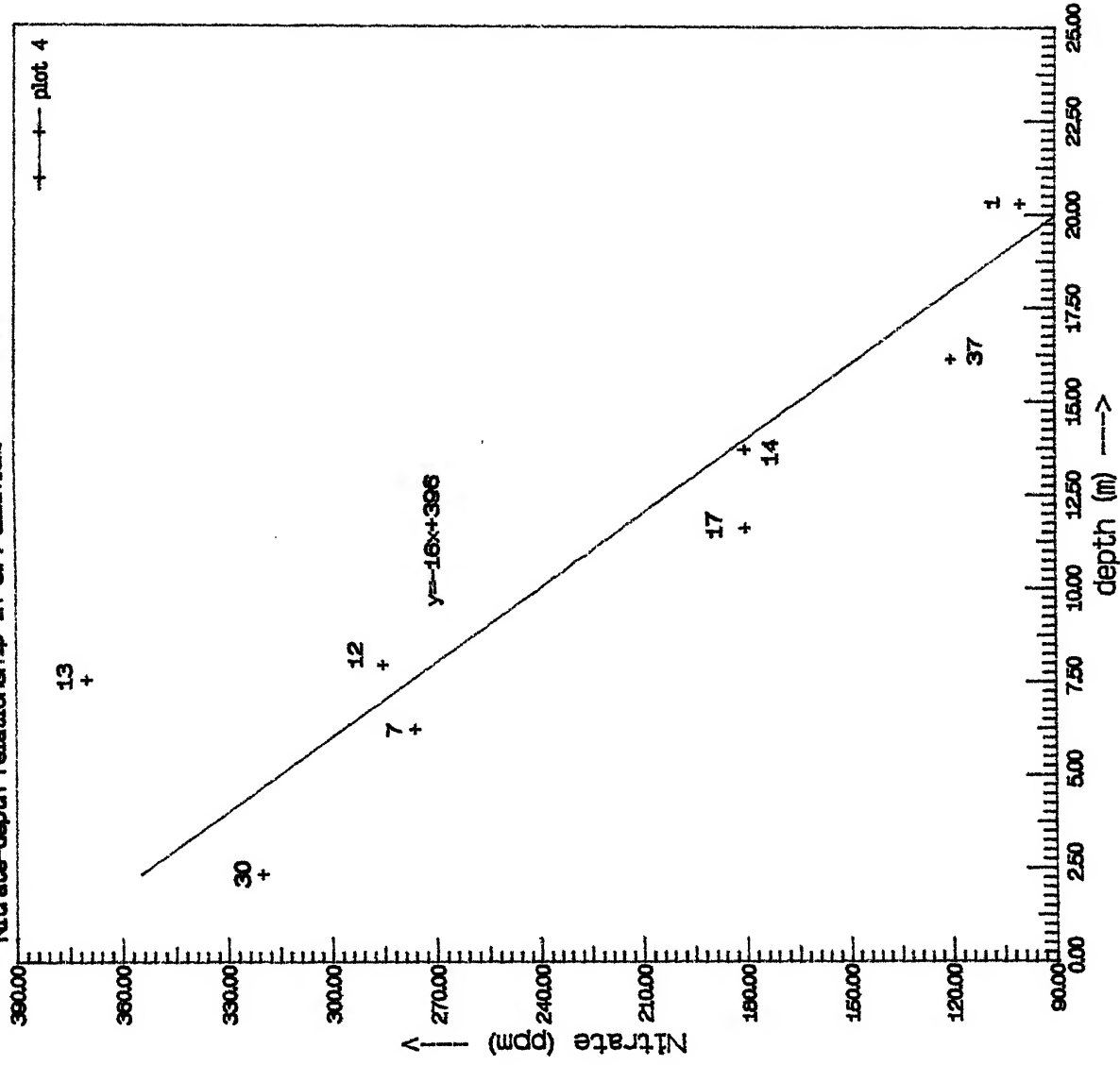
Figure 4.9

Nitrate-depth relationship in U.P. alluvium. (0-25 m)

y=-16x+396

plot 4

Figure 4.10

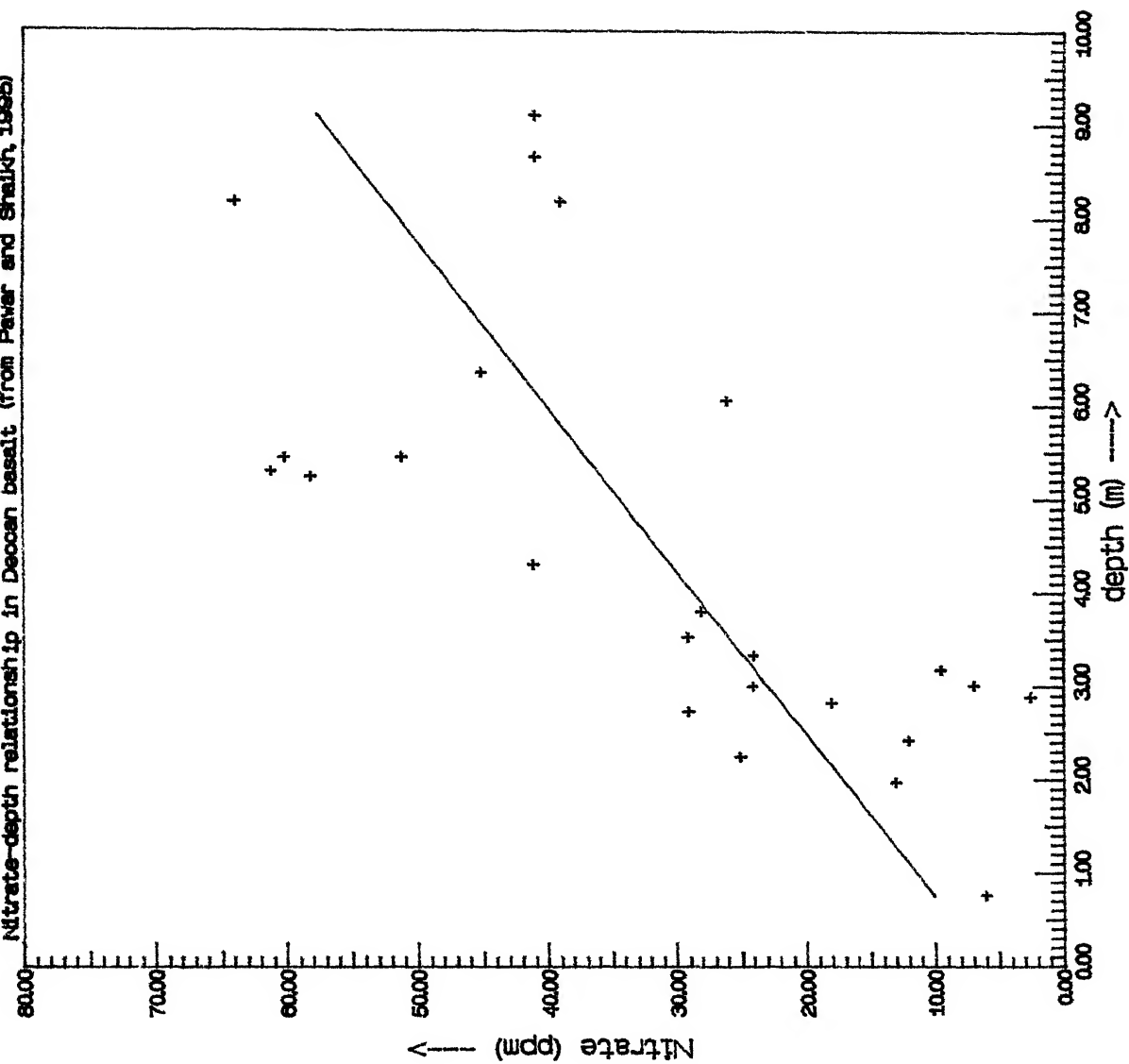Nitrate-depth relationship in Deccan basalt (from Pawar and Shaikh, 1995)
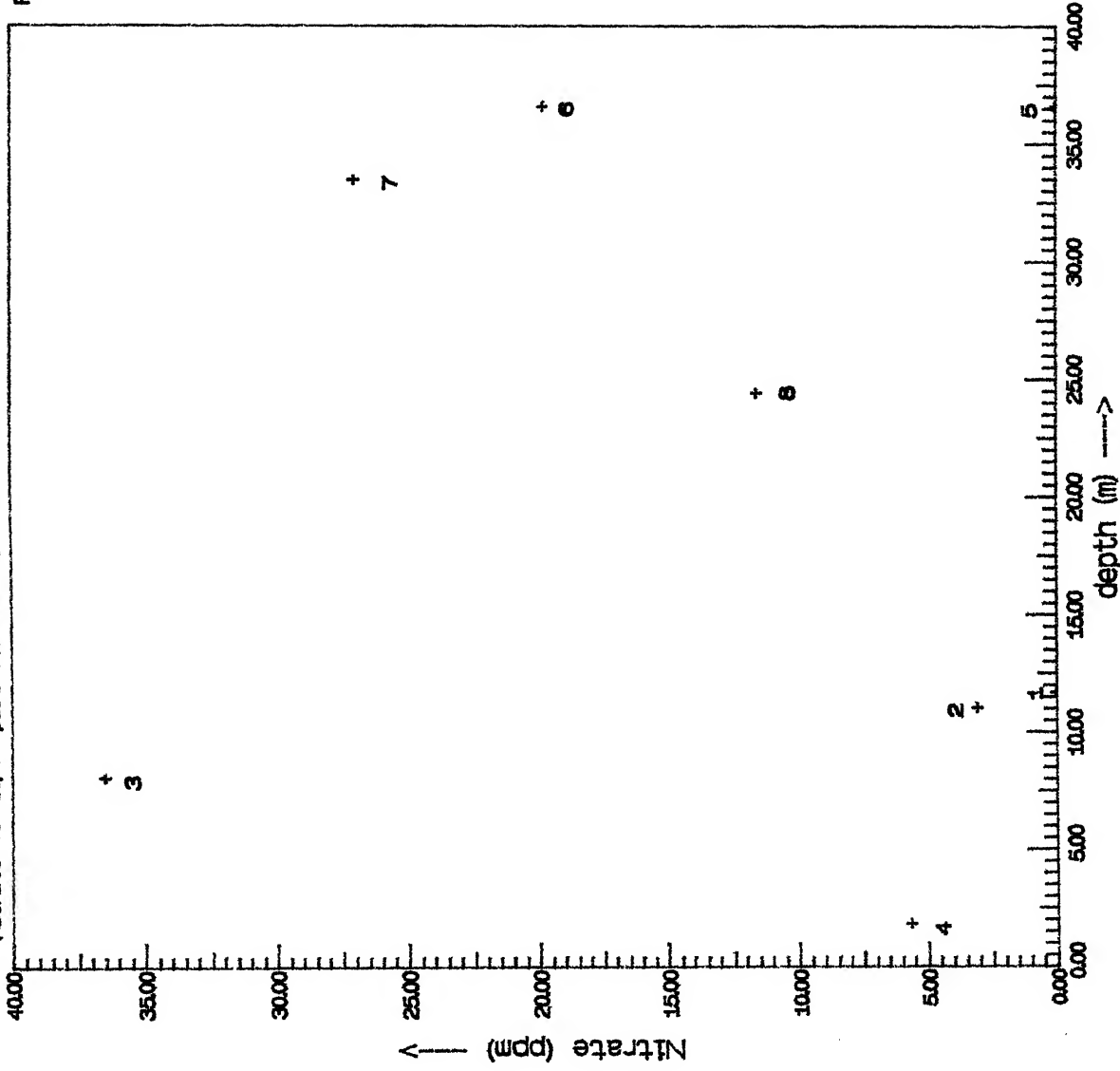
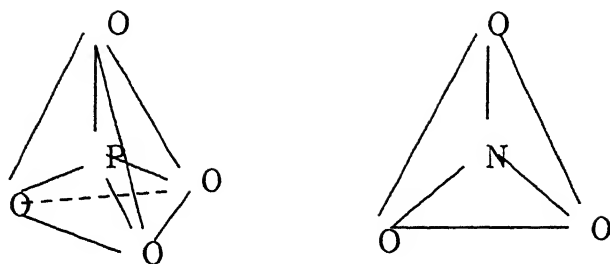Nitrate vs depth plot for wells around IITK

Figure 4.11

USPlot

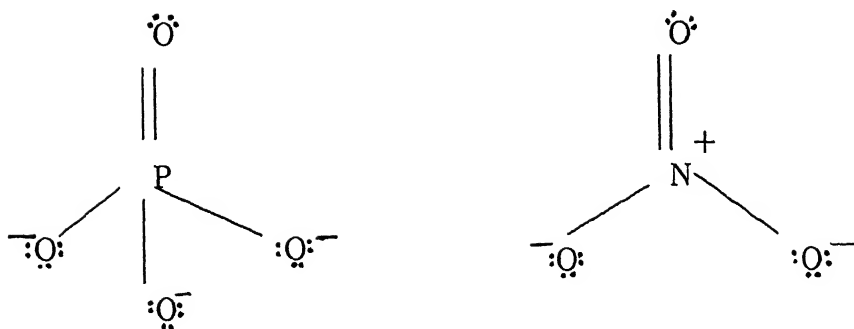Figure 4.12: Molecular structures of phosphate and nitrate

Figure 4.13: Lewis structures of phosphate and nitrate

(d) The mechanism of denitrification is different in aquifers with deeper water table (> 10 m). In this case, oxidizable iron minerals reduce nitrate levels in deeper waters. The contrast in depth relationship was approximately confirmed by the low levels of nitrate in tube-wells in the IITK area as compared with a dug-well in Nankari.

(e) As previous work has indicated that soil minerals participate in anion-exchange with PO_4^{3-}, a few experimental runs were designed to verify that the NO_3^- anion differs in its interaction with soil minerals. The lack of adsorption was explained with the help of the difference in ionic charge, molecular structure and ligand strength.

5.2   Suggestions for future work

- It is advisable to undertake a similar geochemical interpretation of NO_3^- occurrence in ground water by using an expanded data base covering different seasons within a year and several years in succession.

- The results may be more conclusive if the parameters identified during the present work like extent of fertilizer application, nitrate pollution from domestic sewage, depth to water table, mineralogy of the aquifer, etc. are tested at a specific location where all details on the hydrogeological aspects can be easily collected.

- It would be interesting to carry out a modelling exercise on the rate of ground water movement along with the migration of the nitrate front as attempted by Postma and Boesen (1991). For this purpose, tracer studies utilizing tritium isotope can be adopted.

- Isotopic work using $\delta^{15}N$ can be tried out to distinguish between natural soil nitrate and animal waste nitrate (Kreitler and Jones, 1975)

- A major handicap during the work was the non-availibility of a simple method of nitrate analysis at higher concentrations. Other workers have adopted the ion-chromatography method and the nitrate-electrode method, which can be tried out for collecting additional data on nitrate concentration in ground water.

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